Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs. VI. Die Austauschreaktion der Sauerstoffatome zwischen Sauerstoff und Wasserdampf an der Oberfläche der Oxyde von zweiter, vierter und sechster Gruppe des periodischen Systems. 2. Theoretischer Teil.[1]

Von Noriyoshi MORITA.

(Eingegangen am 27. Dezember 1939).

Inhaltsübersicht. Die katalytische Wirksamkeit der Oxyde, die zu II. IV. und VI. Gruppe des periodischen Systems gehören, nämlich der Oxyde von Magnesium, Calcium, Strontium, Barium; Zink, Cadmium; Titan, Zirkonium, Thorium; und Chrom, Molybdän, Wolfram, für die Austauschreaktion der O-Atome zwischen gasförmigem Saurstoff und Wasserdampf an der Oberfläche des resp. Oxyds wird unter Verwendung der im 1. Teil der vorliegenden Versuche gewonnenen Ergebnisse miteinander verglichen. Daraus ergibt sich, dass die Oxyde, die zu IV. Gruppe gehören, innerhalb einer bestimmten Reihe bzw. Periode die geringste Wirksamkeit besitzen. Was die Reihenfolge der Katalytischen Wirksamkeit innerhalb einer bestimmten Gruppe anbetrifft, so liegt die Sache noch nicht so ganz klar wie oben. Aber in einigen Fällen können wir doch eine gewisse Beziehung zwischen der katalytischen Wirksamkeit und Reihennr. der einzelnen Oxyde ausfindig machen. So. z.B. nimmt die Wirksamkeit der Oxyde der Erdalkalimetalle mit zunehmender Reihennr. allmählich zu. Dagegen nimmt die Wirksamkeit der zu VI.-Gruppe angehörigen Oxyde nämlich Cr_2O_3, MoO_3 und WO_3 mit wachsender Reihennr. ziemlich erheblich zu. Plausible Deutung für die so gefundene regelmässige Änderung der katalytischen Wirksamkeit mit der Gruppen- bzw. Reihennr. findet sich am Schluss.

Ermittelung von Temperatur $t(10\%)$. In vorhergehender Mitteil. (Teil 1) werden die Versuchsergebnisse berichtet, die wir bei den Austauschversuchen zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche verschiedener Arten der Oxyde von II. IV. und VI. Gruppe des periodischen Systems gewonnen haben. Deshalb sind wir jetzt in der Lage mit Hilfe des so gewonnenen Versuchsmaterials die katalytische Wirksamkeit der in Rede kommenden Oxyde miteinander zu vergleichen. Zu diesem Zweck werden zunächst die in Teil 1 (in Tabelle 1 bis 12) angegebenen Versuchsergebnisse in nebenstehenden Abbn. 1 bis 3 graphisch wiedergegeben, wo das gefundene Austauschmass $\%A$ gegen die Versuchstemperatur eingezeichnet sind. Dabei entspricht Abb. 1 der in Tabelle 1 bis 5 von 1. Teil angegebenen Versuchsreihe 1 mit den Oxyden von II. Gruppe des periodischen Systems, Abb. 2 der in Tabelle 6 bis 9 angegebenen Versuchsreihe 2 mit den Oxyden von IV. Gruppe und Abb. 3 der in Tabellen 10 bis 12 angegebenen Versuchsreihe 3 mit den Oxyden von VI. Gruppe. Weiter wird die Kurve von CaO in Abb. 1, die von SnO_2-I in Abb. 2, die von Cr_2O_3-I in Abb. 3 werden aus Abb. 1 in IV. Mitteil. und Kurve von SiO_2 aus Tabelle 1 in II. Mitteil. entnommen.

(1) 1. Teil: dies Bulletin, **15** (1940), 47. Vgl. dazu I. Mitteil.: dies Bulletin, **13** (1938), 357; II. Mitteil.: ebenda, **13** (1938), 601; III. Mitteil.: ebenda, **13** (1938), 656; IV. Mitteil.: ebenda, **14** (1939), 9; V. Mitteil.: ebenda, **14** (1939), 520; **15** (1940), 1.

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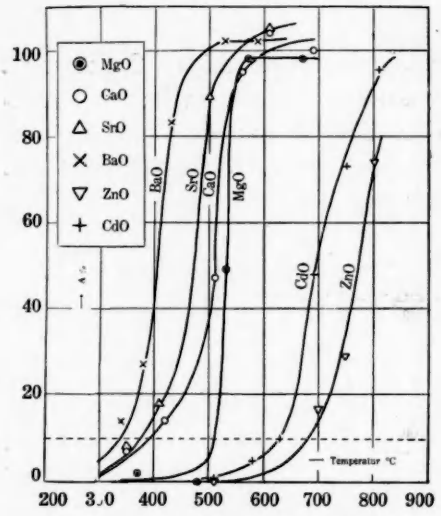

Abb. 1. Die Abhängigkeit des Austauschmasses %A von der Versuchstemperatur bei den Oxyden von II. Gruppe.

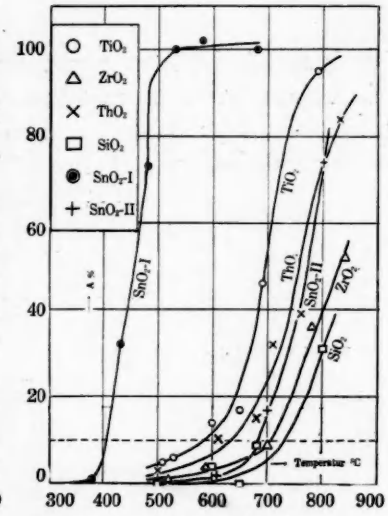

Abb. 2. Die Abhängigkeit des Austauschmasses %A von der Versuchstemperatur bei den Oxyden von IV. Gruppe.

Wenn man aus jeder dieser Kurven in Abbn. 1 bis 3 solch eine Temperatur $t(10\%)$ entnimmt, wo das gefundene Austauschmass %A sich zuerst auf 10% beläuft, erhält man die Zahlenwerte, die in Tabelle 1 unterhalb jeder chemischen Formel der betreffenden Oxyde angegeben sind. Da aber diese Temperatur $t(10\%)$ um so niedriger liegen muss je grösser die katalytische Wirksamkeit des betreffenden Oxyds ist und weiter die Höhe von $t(10\%)$, wie darauf schon in IV. Mitteil. hingewiesen wurde, nicht sehr von den benutzten Versuchsbedingungen beeinflusst wird, darf man wohl mit dieser Temperatur $t(10\%)$ bzw. ihrem reziproken Wert die katalytische Wirksamkeit der Oxyde miteinander vergleichen. Dass diese Temperature $t(10\%)$ für ein bestimmtes Oxyd durch seine Herstellungsmethode nicht stark beeinflusst wird, können wir bei Cr_2O_3 wohl ersehen. In diesem Fall ergeben nämlich die zwei verschiedenen Arten der Präparate, Cr_2O_3-I und Cr_2O_3-II, miteinander

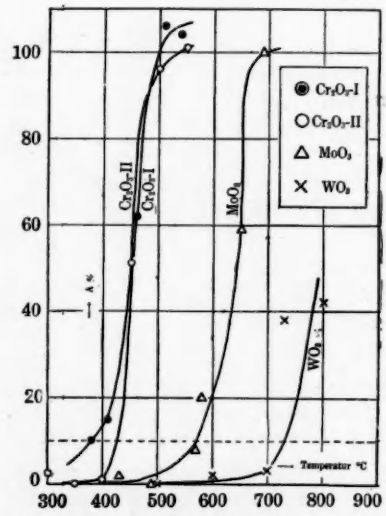

Abb. 3. Die Abhängigkeit des Austauschmasses %A von der Versuchstemperatur bei den Oxyden von VI. Gruppe.

Tabelle 1. Vergleich der katalytischen Wirksamkeit der verschiedenen Oxyde für die Austauschreaktion der O-Atome zwischen Sauerstoffgas und Wasserdampf: $t(10\%)$.

Reihe \ Gruppe	II		IV		VI	
	a	b	a	b	a	b
3	MgO 500			SiO_2 700		
4	CaO 390		TiO_2 590		Cr_2O_3 I, 380 II, 420	
5		ZnO 680		GeO_2 —		
6	SrO 380		ZrO_2 700		MoO_3 570	
7		CdO 630		SnO_2 I, 400 II, 670		
8	BaO 350		CeO_2 —			
10					WO_3 710	
11			ThO_2 640			

eine fast gleich hohe Temperatur $t(10\%)$, obgleich das aus Ammoniumchromat hergestellte Cr_2O_3-II viel voluminöser als das aus Chromhydroxyd gewonnene Cr_2O_3-I aussieht. Nur beim Fall von Zinnoxyd haben wir einen ziemlich grossen Unterschied von $t(10\%)$ zwischen SnO-I und SnO_2-II gefunden. Solch ein grosser Unterschied der katalytischen Wirksamkeit zwischen verschiedenen Arten der Präparate von einem und demselben Oxyd wird aber oft bei solchem Oxyd gefunden, das verhältnismässig kleine katalytische Wirksamkeit besitzt und besonders wenn, wie es vorkommen kann, das Präparat unflüchtige Verunreinigungen wie z.B. unflüchtige Alkali enthält. Deshalb liegt die Annahme sehr nahe, dass es sich dabei meistens um die Promotorwirkung bzw. Mischkatalysatorwirkung der unbewusst eingetretenen Verunreinigungen handelt, worüber später in einer anderen Mittelung ausführlich berichtet werden soll. Zieht man diese Tatsache in Rechnung, dann darf wohl vermutet werden, dass die viel niedrigere Temperatur $t(10\%)$ und folglich grössere Wirksamkeit des einen Präparats SnO_2-I als das andere SnO_2-II von der Promotorwirkung irgendwelcher Verunreinigungen herrühren dürfte, die im ersteren Präparat unbewusst hineingeraten sind. Diese Vermutung liegt aber um so näher, als das erste Präparat SnO_2-I bloss nach starker Erhitzung käuflichen Zinnoxyds direkt zum Versuch verwendet wurde. Aus diesem Grund möchten wir lieber die höhere Temperatur $t(10\%)$

des zweiten Präparats SnO_2-II d.h. 670° als den richtigen Wert für Zinnoxyd vorziehen.

Beziehung zwischen $t(10\%)$ bzw. katalytischer Wirksamkeit und Gruppennummer. Wenn man auf diese Weise jedem Oxyd in Tabelle 1 den ihm eigentlichen Wert von $t(10\%)$ zuschreibt, können wir zwischen der Höhe von $t(10\%)$ und der Stellung des betreffenden Oxyds im periodischen System eine gewisse Beziehung finden. Vergleicht man zunächst den Wert von $t(10\%)$ innerhalb einer bestimmten Reihe (bzw. Periode), so finden wir ebenso wie in IV. Mitteil., dass das Oxyd von IV. Gruppe den grössten Wert von $t(10\%)$ zeigt. Dies weist aber ohne weiteres darauf hin, dass die katalytische Wirksamkeit der Oxyde für die Austauschreaktion der O-Atome zwischen Sauerstoffgas und Wasserdampf bei den Oxyden der IV. Gruppe am geringsten ist und nach beiden Seiten d.h. nach II. und VI. Gruppe allmählich zunimmt. Wir kamen in III. Mitteil. zu dem Ergebnis, dass bei der katalytischen Austauschreaktion an der Oberfläche des Kupferoxyds CuO die aktivierte Adsorption des Wasserdampfes der massgebende Prozess ist. Dagegen berichteten wir in letzter V. Mitteil., dass bei derselben Reaktion an der Oberfläche des Manganoxyds Mn_2O_3 die aktivierte Adsorption des Sauerstoffgases massgebend ist und weiter, dass diese aktivierte Adsorption des Sauerstoffs an Manganoxyd mit dem verhältnismässig hohen Zersetzungsdruck des betreffenden Oxyds bei Versuchstemperaturen in engem Zusammenhang steht. Deshalb liegt nahe im allgemeinen anzunehmen, dass bei den Oxyden, die mindestens bei benutzten Versuchstemperaturen einen kleinen Zersetzungsdruck ausüben aber dementgegen verhältnismässig grosse Hydratisierbarkeit zeigen, wie z.B. CuO, CaO und Al_2O_3, die aktivierte Adsorption des Wasserdampfes, während bei den Oxyden, die verhältnismässig grossen Zersetzungsdruck aber kleine Hydratisierbarkeit zeigen, wie z.B. Mn_2O_3, Cr_2O_3, und MoO_3, die aktivierte Adsorption des Sauerstoffs eine massgebende Rolle spielt. Mithin darf wohl geschlossen werden, dass bei bei solchen Oxyden, an deren Oberfläche infolge kleiner Hydratisierbarkeit und kleinen Zersetzungsdruckes weder die aktivierte Adsorption des Wasserdampfes noch die des Sauerstoffs leicht stattfinden kann, die katalytische Wirksamkeit den Minimumwert zeigen muss. Dies kann gerade der Fall mit den Oxyden der IV. Gruppe sein, weil die zu dieser Gruppe gehörigen Oxyde im allgemeinen schwer hydratisierbar sind, aber zugleich ihr Zersetzungsdruck auch bei ziemlich hohen Temperaturen gewöhnlich sehr klein ist. Auf diese Weise können wir vielleicht das Auftreten des Minimums der katalytischen Wirksamkeit für die in Rede kommende Austauschreaktion bei den Oxyden in IV. Gruppe verständlich machen.

Beziehung zwischen $t(10\%)$ bzw. katalytischer Wirksamkeit und Reihenummer. Was die Reihenfolge der katalytischen Wirksamkeit in einer bestimmten Gruppe anbetrifft, so liegt die Sache nicht so einfach wie oben. Aber wir können doch in einigen Fällen eine ziemlich ausgeprägte Beziehung zwischen der katalytischen Wirksamkeit der Oxyde und ihrer Reihennr. ausfindig machen. So wird z.B. die deutlichste Regelmässigkeit bei den Oxyden der II. Gruppe a d.h. bei den Oxyden der Erdalkalimetalle sowie in VI. Gruppe a d.h. bei den Oxyden von Cr, Mo

und W gefunden. Beim ersten Fall lässt sich leicht ersehen, dass MgO die höchste $t(10\%)$ und folglich die kleinste Wirksamkeit besitzt und die letztere mit zunehmender Reihennr. d.h. von CaO bis BaO allmählich zunimmt. Diese regelmässige Zunahme der katalytischen Wirksamkeit der Erdalkalimetalloxyde mit zunehmender Reihennr. lässt sich vielleicht dadurch deuten, dass die Hydratisierbarkeit dieser Oxyde gerade in dieser Reihenfolge allmählich zunimmt. Das Oxyd von Beryllium BeO, das erste Glied dieser Gruppe, bildet bekanntlich ein Kristallgitter von Wurzittypus und die innerhalb dieses Gitters zwischen einzelnen Atomen herrschende Bindung wird bis zum grössten Teil als Atombindung angenommen. Dementsprechend ist dieses Oxyd sehr schwer hydratisierbar. In diesem Punkt ähnelt das Verhalten des Oxyds des zweiten Gliedes dieser Gruppe, nämlich das von MgO mehr dem ersten Glied BeO als dem darunter liegenden dritten Glied CaO. Obwohl das Kristallgitter von MgO ebenso wie das von CaO und das der Oxyde der anderen höheren Homologe der Gruppe als ein Ionengitter aufgefasst wird, wurde doch von Nakagawa in unserem Laboratorium in einem noch nicht veröffentlichten Versuch gefunden, dass MgO viel schwerer hydratisierbar als CaO ist. Dieser Befund legt uns deshalb die Annahme nahe, dass die kleine katalytische Wirksamkeit von MgO mit dieser geringen Fähigkeit dieses Oxyds zur Hydratbildung in engem Zusammenhang steht. Die ähnliche Neigung der abnehmenden $t(10\%)$ d.h. der zunehmenden katalytischen Wirksamkeit mit der wachsenden Versuchsnr. lässt sich auch in II. Gruppe b, d.h. bei ZnO und CdO erkennen. Aber weil in diesem Fall erstens das Versuchsmaterial noch ziemlich wenig und zweitens der Unterschied von $t(10\%)$ zwischen beiden untersuchten Oxyden nicht so ausgeprägt ist, können wir noch nichts so Bestimmtes sagen. Aber in jedem Fall liegt die Vermutung nahe, dass der Unterschied der katalytischen Wirksamkeit zwischen einzelnen Oxyden in Subgruppe b, d.h. zwischen den zur Nebenreihe gehörigen Oxyden, im allgemeinen nicht so ausgeprägt sein dürfte als bei den Oxyden, die zu Subgruppe a bzw. Hauptreihe des periodischen Systems gehören.

Die zweite verhältnismässig deutliche Reihenfolge der katalytischen Wirksamkeit lässt sich bei den Oxyden in VI. Gruppe a nämlich bei Cr_2O_3, MoO_3 und WO_3 finden. In diesem Fall nimmt aber die katalytische Wirksamkeit der Oxyde, gerade im Gegenteil als bei den oben beschriebenen Alkalierdmetallen, mit zunehmender Reihennr. ziemlich stark ab, wie man dies aus der zunehmenden $t(10\%)$ der Oxyde mit der Reihennr. ersieht (vgl. Tabelle 1.) Nimmt man nun an, wie darauf schon oben hingewiesen wurde, dass der massgebende Prozess bei der katalytischen Austauschreaktion an der Oberfläche dieser Arten der Oxyde ebenso wie bei Mn_2O_3 die aktivierte Adsorption des Sauerstoffs ist, so stimmt die oben gefundene Reihenfolge der katalytischen Wirksamkeit gerade mit der der Reduzierbarkeit der Oxyde der in Rede kommenden Metalle gut überein. Denn nach der chemischen Erfahrung ist wohl bekannt, dass die unter den gewöhnlichen Versuchsbedingungen stabilste Form des Oxyds jedes in Rede kommenden Metalls resp. Cr_2O_3, MoO_3 und WO_3 ist und weiter, dass unter den letzteren zwei Arten der Oxyde MoO_3 und WO_3 das letztere eine grössere Bildungswärme besitzt als das erstere.

Die Reihenfolge der katalytischen Wirksamkeit der Oxyde von IV. Gruppe ist nicht so einfach und klar wie bei den erwähnten beiden Gruppen II und VI. Obwohl auch in dieser Gruppe IV ein viel geringerer Unterschied der katalytischen Wirksamkeit innerhalb der Subgruppe b d.h. zwischen SiO_2 und SnO_2[2] als bei den Oxyden der Subgruppe a d.h. zwischen TiO_2, ZrO_2 und ThO_2 gefunden wird, ist die Reihenfolge der katalytischen Wirksamkeit zwischen den letzt genannten drei Oxyden in Subgruppe a ganz unregelmässig; das erste Glied TiO_2 besitzt die grösste katalytische Wirksamkeit, dann folgt das letzte Glied ThO_2 und das zweite Glied ZrO_2 zeigt die geringste Wirksamkeit. Aber über diese gefundene Unregelmässigkeit in IV. Gruppe a können wir ohne weiteres nichts Bestimmtes sagen, bis weitere Versuche ausgeführt werden, erstens weil der gefundene Unterschied der katalytischen Wirksamkeit bzw. der Temperatur $t(10\%)$ nicht so deutlich ist und zweitens weil die katalytische Wirksamkeit eines gegebenen Oxyds, wie darauf schon oben hingewiesen wurde, manchmal durch die Beimengung verhältnismässig geringer Mengen Verunreinigungen ziemlich stark beeinflusst wird.

Herrn Prof. Dr. T. Titani möchte ich für sein warmes Interesse an dieser Arbeit bestens danken. Der Nippon-Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkohkai (der Hattori-Stiftung), die durch Gewährung des Stipendiums die Ausführung der vorliegenden Arbeit ermöglicht haben, bin ich auch zu grösstem Dank verpflichtet.

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Kagaku Kyositu
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Vergleichung der Dichte des Wassers aus verschiedenen Orten auf der Erde.[1]

Von **Kokiti GOTO** und **Kenzo OKABE.**

(Eingegangen am 29. Januar 1940).

Inhaltsübersicht. Die Dichte des Wassers aus verschiedenen Orten auf der Erde innerhalb und ausserhalb Japans wird nach gründlicher Reinigung untereinander schwebemetrisch verglichen. Dabei kommt man zu der Feststellung, dass sie innerhalb des geschätzten Messfehlersbereiches ($\pm$ 0.5γ) untereinander gut übereinstimmt. Aus diesem Grunde darf wohl geschlossen werden, dass alle diese untersuchten Arten von Wasser fast dieselbe Isotopenzusammensetzung besitzen. Die Orte, wo die Probewasser

(2) Bei diesem Vergleich wird t (10%) von SnO_2-II d.h. 670°C aus dem schon oben angegebenen Grunde verwendet.

(1) Abgekürzte Übersetzung der japanischen Mitteilungen *J. Chem. Soc. Japan*, **60** (1939), 705, 707.

gesammelt werden, sind folgende 28: (innerhalb von Japan) Osaka, Muroran, Niigata, Tokuyama, Moji, Kagosima, Kiirun (Keelung), Takao, (ausserhalb von Japan) Hongkong, Cebu in Philippine, Manila, Singapore, Bangkok, Colombo, Bombay, Monbassa in Africa, New York, Cambridge in Ma. U.S.A., Hopewell in Va. U.S.A., Galveston in Tex. U.S.A., Houston in Tex. U.S.A., Panamakanal, Los Angeles in Calf. U.S.A., San Pedro in Calif. U.S.A. und Tacoma in Wash. U.S.A.

Einleitung. Bei den Versuchen mit schwerem Wasser und besonders bei den Untersuchungen über die Isotopenzusammensetzung des Wassers aus verschiedenen natürlichen Ursprüngen nimmt man gewöhnlich die Dichte bzw. die Isotopenzusammensetzung des Leitungswassers bei jedem betreffenden Ort als den Eichpunkt. Aus diesem Grunde ist es höchst wünschenswert die Dichte des Leitungswassers von verschiedenen Orten auf der Erde direkt bzw. indirekt miteinander zu vergleichen. Über die mittelbare Vergleichung der Dichte des Wassers aus verschiedenen Orten fehlen bisher auch keine Versuche. So wird z.B. durch die Versuche einiger Autoren festgestellt, dass das Kristallisationswasser von ein- und demselben natürlichen Mineral dem Leitungswassers aus verschiedenen Orten auf der Erde gegenüber immer fast denselben Dichteüberschuss ergibt.[2] Diese Ergebnisse weisen aber offensichtlich darauf hin, dass die in Rede kommenden Arten Leitungswasser miteinander fast dieselbe Dichte bzw. Isotopenzusammensetzung besitzen. Aber was den unmittelbaren Vergleich der Dichte des Leitungswassers aus verschiedenen Orten auf der Erde anbetrifft, so sind bis jetzt, wenigstens so weit unsere Kenntnisse reichen, keine ausführlichen Versuche veröffentlicht worden.[3] Von diesem Gesichtspunkt aus hat Dr. K. Yamasaki vom chemischen Institut der Kaiserlichen Universität Tokio mit Unterstützung der Frachtabteilung der Mitsui Bussan Kaisha (Mitsui Handelsgesellschaft) verschiedene Arten von Leitungswasser gesammelt und die so gesammelten Wasserarten uns alle zur Verfügung gestellt. Die vorliegenden Versuche wurden deshalb unter Verwendung dieser Arten von Leitungswasser durchgeführt. Die dabei benutzte Versuchsmethode ist prinzipiell ganz einfach; das betreffende Wasser wird zunächst möglichst gründlich gereinigt und dann die Dichte des so gereinigten Wassers mittels eines gut bewährten Quarzschwimmers mit der des ebenfalls sorgfältig gereinigten Osaka-Leitungswassers verglichen. Da bei dieser

(2) Das Kristallisationswasser von Tincal ($Na_2B_4O_7 \cdot 10H_2O$) aus Californien zeigt dem Leitungswasser von Osaka, Washington und London gegenüber einen Dichteüberschuss von 2γ, 3γ und 0γ. Auf ähnliche Weise besitzt das Kristallisationswasser von Rasorit ($Na_2B_4O_7 \cdot 4H_2O$) desselben Ursprungs dem Osaka-, Washington- und London-Leitungswasser gegenüber einen Dichteüberschuss von 4γ, 7γ und 6γ und das von Carnalit aus Stassfurt dem Osaka- und London-Leitungswasser gegenüber einen Dichteüberschuss von 2γ und 3γ. Vgl. E. W. Washburn und E. R. Smith, *Bur. Standard J. Research*, **12** (1934), 305 ; H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell und H. V. A. Briscoe, *J. Chem. Soc.*, **1934**, 1207, 1948. Die Daten über den Vergleich mit dem Osaka-Leitungswasser wird aus dem nicht veröffentlichten Versuch von T. Titani und M. Koizumi entnommen.

(3) T. Titani und N. Morita sowie C. H. Greene und R. J. Voskuyl haben gefunden, dass das Osaka-Leitungswasser nur um 0.2γ bzw. 0.07γ dichter als das Cambridge-Leitungswasser ist. Vgl. T. Titani und N. Morita, *J. Chem. Soc. Japan*, **58** (1937), 1151 und dies Bulletin, **13** (1938), 409. Die umfangreiche Mitteilung von Greene und Voskuyl ist erst nach der Veröffentlichung der japanischen Mitteilung der vorliegenden Arbeit in unsere Hände gelangt. Vgl. den Nachtrag am Ende der vorliegenden Mitteilung.

Art der Versuche die Reinheit des zu untersuchenden Wassers der wesentlichste Faktor bildet, so haben wir darauf die grösste Sorgfalt verwendet.

Reinigung des Wassers. Die uns zur Verfügung gestellten Wasserproben sind alle in Glasflaschen mit Gummi- bzw. Korkstöpsel aufbewahrt worden. Aus diesen Flaschen werden nun bei den Versuchen mit dem Wasser japanischen Ursprungs immer 200 ccm dagegen bei den anderen Arten von Wasser 50 ccm herausgegossen und dem Reinigungsprozess unterworfen. Dieser besteht aber aus folgenden vier Prozessen, die mit ein- und demselben Probewasser nacheinander durchgeführt werden.

(1) Das Wasser wird zunächst in Dampfform über erhitztes Kupferoxyd bis auf etwa 450° geleitet, um dadurch schwer angreifbare Verunreinigungen vollständig oxydiert zu zersetzen. Das dabei benutzte Kupferoxyd wird aber aus reduzierten Kupferdrähtchen und dem Sauerstoffgas aus der Elektrolyse des Osaka-Leitungswassers hergestellt. Diese letztere Massnahme wird deshalb vorgenommen, um dadurch die Veränderung der Isotopenzusammensetzung des behandelten Wassers wegen der eventuell aufzutretenden Austauschreaktion der O-Atome zwischen Wasserdampf und festem Kupferoxyd möglichst zu vermeiden.[4] Diese bis zu einem gewissen Grad derbe Methode der Reinigung wird aber nur für verhältnismässig stark verunreinigte Wasserproben verwendet (Nr. 15, 20, 21, 22, 24, 27 und 28 in unterstehender Tabelle 3).[5] Die sonstigen nicht so stark verunreinigten Wasserproben werden dagegen ohne weiteres dem nächsten Reinigungsprozess (2) unterworfen.

(2) Bei diesem Prozess wird das Wasser aus dem oben angegebenen Prozess (1) bzw. die frische Wasserprobe aus der Flasche (vgl. oben) unter Zusatz von möglichst wenigen Mengen KOH und $KMnO_4$ in einem mit Rückflusskühler versehenen Kolben so lange sieden gelassen, bis die oxydierbaren Verunreinigungen im Wasser als restlos zersetzt angesehen werden können. So dauerte Prozess (2) mit den Proben Nr. 1 8 bis 12 Stunden, mit Nr. 9 bis 26 und Nr. 28 3 bis 6 Stunden, dagegen mit der Probe Nr. 27, die verhältnismässig stark verunreinigt war, sogar 100 Stunden lang.

(3) Das Destillat aus dem Prozess (2) wird unter Zusatz von wenigen Mengen P_2O_5 und $KMnO_4$ abdestilliert.

(4) Das Destillat aus dem Prozess (3) wird unter Zusatz von möglichst wenigen Mengen $Ba(OH)_2$ in einem Kohlensäure-, Feuchtigkeit- und staubfreien Luftstrom abdestilliert.

(5) Das aus dem Prozess (4) erhaltene Destillat wird schliesslich ohne jeden Zusatz aber ebenfalls in einem gereinigten Luftstrom durch den Quarzkühler abdestilliert.

Bei jeder dieser Stufe der Destillationen wird immer 0.5 ccm aus dem Anfangsdestillat entfernt und nach der Beendigung der Destillation wird dieselbe Menge (0 5 ccm) Wasser im Kolben zurückgelassen. Diese Massnahmeregel ist offensichtlich insofern nötig, um die Veränderung der Dichte des Wassers wegen der isotopischen Fraktionierung bei der

(4) Vgl, N. Morita, dies Bulletin, **13** (1938), 656.

(5) Der grösste Teil dieser Verunreinigungen dürfte während der Aufbewahrung des Wassers in Flaschen hauptsächlich durch Gummi- bzw. Korkstöpsel verursacht worden sein.

Destillation für alle untersuchten Arten von Wasser möglichst gleich zu halten.[6]

Bestimmung der Dichte des Wassers. Die Dichte des so gereinigten Wassers wird unter Benutzung eines Quarzschwimmers mit der des auf genau dieselbe Weise gereinigten Osaka-Leitungswassers verglichen. Der dabei benutzte Quarzschwimmer ist im hiesigen Laboratorium schon paar Jahre lang in Gebrauch und deshalb gut geartelt.[7] Die Dichtebestimmung mittels dieses Quarzschwimmers führt man nach der von Koizumi[8] entwickelten Methode bei 9.5° durch, indem man den Unterschied ΔT der Gleichgewichtstemperatur zwischen der betreffenden Wasserprobe und dem Standardwasser (Osaka-Leitungswasser) mittels eines Beckmannthermometers abliest und aus dem so gefundenen Temperaturunterschied ΔT den Dichteunterschied Δs nach Gl. (1) berechnet:

$$\Delta s = -79\Delta T \qquad (1).$$

Zu dieser Dichtebestimmung wird aber das Wasser aus dem oben erwähnten Reinigungsprozess (4) ohne weiteres d.h. ohne Entfernung der gelösten Luft verwendet. Deshalb wird das Wasser immer mit Luft gesättigt. Der Fehler wegen der Schwankungen des Sättigungsgrades der Luft in den einzelnen untersuchten Wasserproben darf wohl unberücksichtigt bleiben, weil jedes Wasser, wie schon oben erwähnt wurde, unter möglichst gleichen Versuchsbedingungen gereinigt wird. Nach den Versuchen von Titani und Morita über die Vergleichung der Dichte des Osaka- und Cambridge-Leitungswassers wird der Fehler wegen dieser Schwankung des Sättigungsgrades der Luft in untersuchtem Wasser kleiner als $\pm 0.2\ \gamma$ geschätzt.[6] Diese Grösse liegt aber schon innerhalb des eben zu erwähnenden gesamten Messfehlerbereiches der vorliegenden Versuche.

Die Dichtebestimmung eines angegebenen Probewassers wird jedesmal zwei bis fünfmal wiederholt, indem man untereinander ganz unabhängig gereinigte frische Proportionen des Wassers verwendet. Die dabei gefundenen einzelnen Werte von Δs ein- und desselben Probewassers schienen aber höchstens innerhalb $\pm 0.5\ \gamma$ untereinander gut übereinzustimmen, wie man dies aus den in Tabelle 1 angegebenen Musterversuchen mit Kagosima-Leitungswasser ersieht.

Tabelle 1. Versuchsergebnisse mit Kagosima-Leitungswasser.

Versuchsnr.	ΔT	Δs in γ	Mittel
1	−0.005	+0.40	
2	−0.003	+0.24	
3	−0.006	+0.48	+0.40
4	−0.007	+0.56	
5	−0.004	+0.32	

(6) N. Morita, *J. Chem. Soc. Japan*, **58** (1937), 1151. Vgl. dazu T. Titani und N. Morita, dies Bulletin, **13** (1938), 409.

(7) Derselbe Schwimmer, den Titani und Morita zur Vergleichung der Dichte des Leitungswassers von Osaka und Cambridge benutzt haben. Vgl. Fussnote (6).

(8) M. Koizumi, *J. Chem. Soc. Japan*, **56** (1935), 811. Vgl. auch Y. Shibata, K. Noguchi und O. Kaneko, dies Bulletin, **14** (1939), 275.

Aus diesen Ergebnissen darf man wohl zu dem Schluss kommen, dass der Messfehlerbereich der vorliegenden Versuche höchstens innerhalb $\pm 0.5\ \gamma$ liegt. Dabei wird offensichtlich auch der Fehler wegen der unvollständigen Reinigung (isotopische Fraktionierung u.s.w.!) mitberechnet.[9] Weil die einzelnen Werte von Δs ein- und desselben Probewassers untereinander so gut übereinstimmten, geben wir in weiter unten angegebenen Tabellen 2 und 3 nur den Mittelwert von Δs für jedes Probewasser wieder.

Versuchsergebnisse. Die in den vorliegenden Versuchen gewonnenen Ergebnisse sind in Tabelle 2 und 3 zusammengestellt, wo das Datum in der letzten Spalte die Zeit angibt, als die betreffende Wasserprobe ange-

Tabelle 2. Dichteüberschuss Δs des Leitungswassers aus verschiedenen Orten in Japan dem Osaka-Leitungswasser gegenüber.

Nr.	Leitungswasser	ΔT	Δs in γ	Datum
0	Osaka	±0.000	±0.0	—
1	Tokio	—	+0.4	—
2	Muroran	−0.003	+0.2	1936. 3. 29.
3	Niigata	−0.005	+0.4	„ 5. 11.
4	Tokuyama	−0.004	+0.3	„ 4. 11.
5	Moji	−0.003	+0.2	„ 4. 20.
6	Kagosima	−0.005	+0.4	„ 2. 17.
7	Kiirun (Keelung)	−0.003	+0.2	„ 6. 8.
8	Takao	+0.001	−0.1	„ 2. 1.

Tabelle 3. Dichteüberschuss Δs des Leitungs-,Quellen- bzw. Kanalwassers aus verschiedenen Orten auf der Erde dem Osaka-Leitungswasser gegenüber.

Nr.	Ort	Art des Wassers	ΔT	Δs in γ	Datum
0	Osaka	Leitungswasser	±0.000	±0.0	—
9	Hongkong	„	—	±0.0	1936. 4. 13.
10	Manila	„	—	+0.1	„ 4. 28.
11	Cebu in Philippinen	„	—	+0.1	„ 4. 30.
12	Singapore	„	—	+0.4	„ 3. 3.
13	Bangkok	„	—	+0.6	„ 5. 10.
14	Colombo	„	—	±0.0	„ 4. 4.
15	Bombay	„	+0.006	−0.5	„ 5. 20.
16	Mombassa in Africa	„	—	±0.0	„ 3. 24.
17	New York	„	—	−0.6	„ 2. 26.
18	Cambridge in Ma. U. S. A.	„	—	+0.2	„ 12. 22.
19	Hopewell in Va. U. S. A.	„	—	−0.2	„ 2. 29.
20	Norfolk in Va. U. S. A.	Quellenwasser	−0.006	+0.5	„ 1. 2.
21	Jacksonville in Flor. U. S. A.	Leitungswasser	−0.007	+0.6	„ 3. 6.
22	Corpus Christi in Tex. U. S. A.	„	−0.007	+0.6	„ 1. 7.
23	Galveston in Tex. U. S. A.	„	—	+0.6	„ 1. 6.
24	Houston in Tex. U. S. A.	„	−0.008	+0.6	„ 1. 14.
25	Panamakanal	Kanalwasser	—	+0.4	„ 3. 11.
26	Los Angeles in Calf. U. S. A.	Leitungswasser	−0.007	+0.6	„ 3. 20.
27	San Pedro in Calf. U. S. A.	„	+0.009	−0.7	„ 3. 30.
28	Tacoma in Wash. U. S. A.	„	—	+0.4	„ 5. 11.

(9) Der Fehlerbereich der Schwimmermethode an sich selbst ist selbstverständlich viel kleiner als dies.

sammelt wurde. Weiter wird das Ergebnis mit Tokio-Leitungswasser aus dem unveröffentlichten Versuch von Dr. Koizumi und das von Cambridge-Leitungswasser aus dem Versuch von Titani und Morita[6] entnommen.

Zusammenfassung und Diskussion. Aus den oben in Tabelle 2 und 3 angegebenen Versuchsergebnissen zu urteilen, erscheint das Wasser amerikanischen Ursprungs im allgemeinen um ein wenig dichter als das von japanischem Ursprunge zu sein. Aber auch wenn dieser Dichteunterschied wirklich vorhanden wäre, hätten wir es damit hauptsächlich mit dem Unterschied des Gehaltes des betreffenden Wassers an schwerem Sauerstoff zu tun, weil der Gehalt des natürlichen Wassers an schwerem Sauerstoff viel grösser ist als der an schwerem Wasserstoff und infolgedessen die minimale Schwankung des ersteren viel grösseren Effekt auf die Dichte des Wassers ausübt als die des letzteren. Aber weil in jedem Fall der gefundene Dichteunterschied bei dem vorliegenden Versuche kaum ausserhalb des geschätzten Messfehlerbereiches ($\pm$ 0.5 γ) liegt, möchten wir lieber annehmen, dass die untersuchten Arten von Wasser mindestens mit der Genauigkeit von $\pm$ 0.5 γ alle fast dieselbe Dichte und folglich dieselbe Isotopenzusammensetzung besitzen.

Nachtrag zur Übersetzung. Gleich nach der Veröffentlichung der originalen japanischen Mitteilungen der vorliegenden Versuche ist die ausgezeichnete Arbeit von Greene und Voskuyl[10] eingetroffen. Verfasser fanden in diesen Versuchen gut übereinstimmend mit den vorliegenden Versuchsergebnissen, dass das sorgfältig gereinigte Leitungswasser von Cambridge, Osaka, London, Columbus und Washington jedes mit der Genauigkeit von 0.1 γ dieselbe Dichte besitzt.

Zum Schluss sprechen wir Herrn Dr. K. Yamasaki und der Frachtabteilung der Mitsui Bussan Kaisha für ihre freundliche Überlassung der in den vorliegenden Versuchen benutzten Probewasser unseren verbindlichsten Dank aus. Der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der Wissenschaftlichen Forschungen) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung und Herrn Prof. T. Titani für seine Anregung zu dieser Arbeit sind wir auch zu bestem Dank verpflichtet.

Osaka Teikoku Daigaku Rigaku-bu
Kagaku Kyositu
(Chemisches Institut der wissenschaftlichen Fakultät der Kaiserlichen Universität Osaka)
und Kobe Jogakuin (Kobe Women's College).

(10) G. N. Greene und R. J. Voskuyl, *J. Am. Chem. Soc.*, **61** (1939), 1342.

Properties of Mercury Oxide as an Active Material of Positive Electrode in Alkaline Storage Cell.

By Kyôji KINOSHITA.

(Received January 18, 1940).

(1) *Experiments with red mercury oxide.* The author has reported that the positive and the negative electrode plates of the alkaline storage cell can be prepared with silver oxide[1] and bismuth oxide[2] respectively in pasted form. In the present paper, the results of similar experiments with mercury oxide will be reported.

When red mercury oxide is mixed with 5NNH_4OH solution, a paste-like material will be obtained such as we get in kneading lead oxide with dilute sulphuric acid. We shall call this material "paste" throughout the present report. The electrode plate was prepared by applying this paste to the grids made of nickel plated lead antimony alloy (the size of the grid being about 6.0 cm. × 1.5 cm. × 0.3 cm.) which can also be used for preparing the lead accumulator plate. When the plate thus prepared was dipped into 20% KOH solution a small amount of the active material fell off from the surface. This seemed to happen owing to the poor cohesive power of the active material made of mercury oxide. Similar experiments were undertaken therefore, with the electrode plate which was made by the paste produced by mixing silver oxide and red mercury oxide.

Table 1 shows the properties of the plate used for the experiments.

Table 1.

Number of electrode plate	Amount of active material w (in gram)	Composition of Paste		Weight of grid (in gram)
		Amount of Ag_2O mixed (in gram)	Amount of HgO mixed (in gram)	
6	9.63	—	10.00	15.26
8	5.22	4.00	2.00	15.98
9	6.20	3.75	3.75	15.04
10	6.98	2.00	6.00	16.66

After the paste was applied to the grids, they were left to dry for about 72 hours, then they were dipped into 20% KOH solution. There was no falling off of the active material in any electrode plate.

Electrolytical "formation" of the pasted plate thus obtained were undertaken in 20% KOH solution by the current of 80 milliamperes for

(1) K. Kinoshita, this Bulletin, **12** (1937), 164, 366.
(2) K. Kinoshita, this Bulletin, **15** (1940), 59.

about 90 hours. With the completion of the formation, the positives were combined with the negative electrode of the Nife's accumulator which had already been fully charged, and were subjected to four cycles of charges and discharges by the current of 250 milliamperes. Table 2 shows the results of the experiments.

Table 2.

Number of discharge n	Number of electrode plate					
	No. 8		No. 9		No. 10	
	Discharge hour (in hour)	Capacity C. (in ampere-hours	Discharge hour (in hour)	Capacity C. (in ampere-hours	Discharge hour (in hour)	Capacity C. (in ampere-hours)
1	7.266	1.817	7.833	1.958	8.216	2.054
2	5.500	1.375	6.333	1.583	6.166	1.542
3	5.183	1.296	6.466	1.617	5.633	1.408
4	5.166	1.292	6.500	1.625	5.916	1.479
mean		1.445		1.696		1.621

The voltage of the accumulator No. 6 has fallen to zero at fifteen minutes after the starting of the discharge, so that it was left out from discharging afterwards.

As shown in Table 2, the discharge capacity is comparatively large for each accumulator in the first discharge, but falls remarkably in the second discharge, then it tends to fall continuously.

Fig. 1 shows the discharge characteristic curve in the first discharge.

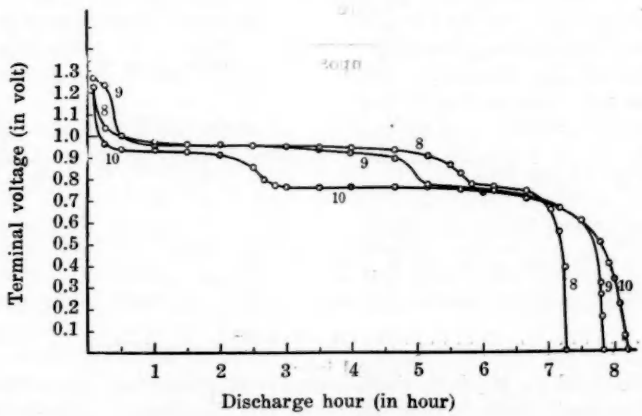

Fig. 1.

As shown in the figure, the voltage falls in two stages the first stage being about 0.95 volt and the second about 0.75 volt. The cell No. 9 gives at the beginning of discharge, the value of over 1.2 volts. Now,

the whole discharge capacity C, is devided into two parts C_1 and C_2, at the inflexion points of the voltage curve between these two stages. The results are given in Table 3.

Table 3.

Number of discharge n	Number of electrode plate					
	No. 8		No. 9		No. 10	
	capacity C_1 (in ampere-hours)	capacity C_2 (in ampere-hours)	capacity C_1 (in ampere-hours)	capacity C_2 (in ampere-hours)	capacity C_1 (in ampere-hours)	capacity C_2 (in ampere-hours)
1	1.417	0.400	1.242	0.717	0.667	1.388
2	0.983	0.392	0.875	0.708	0.317	1.225
3	1.000	0.296	0.908	0.708	0.292	1.117
4	0.863	0.429	1.008	0.617	0.333	1.146
mean	1.066	0.379	1.008	0.688	0.402	1.219

By examining more closely the discharge characteristic curve of Fig. 1, we know, that the variation in the terminal voltage is much like that of silver oxide positives in the pasted form, which the author has previously noticed.[1] When the silver oxide plate combined with the negative electrode of the Nife accumulator was discharged in 20% KOH solution with the same rate of the discharge current, the terminal voltage of about 0.95–0.99 volt was obtained.

Moreover, the terminal voltage of about 1.2 volts at the beginning of the discharge for the cell No. 9 in this experiments was also observed in the case of the silver oxide electrode. This is understood as the discharge capacity obtained by the chemical changes of silver peroxide into silver oxide. The discharge capacity shown in Fig. 1, C_1, therefore, may be resulted from the discharge of the silver oxide which has been mixed in the active material of the electrode.

The following shows the amount of the silver oxide and the mercury oxide in the active material of the electrode, which has been calculated from Table 1.

Number of the electrode plate...		No. 8	No. 9	No. 10
Amount of silver oxide (g.) ..	W_s	3.48	3.10	1.74
Amount of mercury oxide (g.)	W_m	1.74	3.10	5.24
Total	w	5.22	6.20	6.98

The values of C_1/W_s have been calculated assuming that the discharge of the first stage is resulted from the discharge of silver oxide, and are shown in Table 4. In this table the values of C_2/W_m are also shown for comparison.

This table shows that the value of C_1/W_s is the same as, or a bit smaller than, that of the alkaline storage cell in the pasted form consisting of silver oxide alone, which was determined previously by the author.[1]

Table 4.

Number of discharge n	Number of electrode plate					
	No. 8		No. 9		No. 10	
	C_1/W_s in ma. h./g.	C_2/W_m in ma. h./g.	C_1/W_s in ma. h./g.	C_2/W_m in ma. h./g.	C_1/W_s in ma. h./g.	C_2/W_m in ma. h./g.
1	414	230	401	231	383	265
2	284	225	282	228	182	234
3	287	170	294	228	168	213
4	248	246	325	199	191	219
mean	311	218	326	222	231	233

The value of C_1/W_s decreases as the amount of HgO increases, while the value of C_2/W_m does not change so much with the variation of the content of Ag_2O.

Now, plotting C_1 or C_2 in ordinate (in amperehour) and W_s or W_m in abscissa (in gram) we obtain Fig. 2 and Fig. 3.

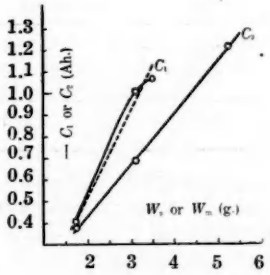

Fig. 2.

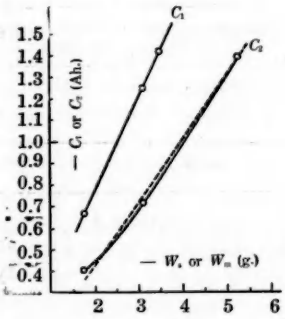

Fig. 3.

In Fig. 2 the average value of the four discharges is used for each of C_1 and C_2, and in Fig. 3 the result of the first discharge is used for each of C_1 and C_2. As can be seen from Fig. 2, there is a linear relation between C_2 and W_m, while no such relation between C_1 and W_s. From Fig. 3, both C_1 and C_2 may be presumed as linear. However, all these have only three measuring points and the relation cannot accurately be brought out.

In calculating the value of C_1, in the case of such electrode as No. 9 which shows the characteristic curve that seems to result owing to the reaction $Ag_2O_2 \rightarrow Ag_2O$, should be left out from the calculation.

(2) *Experiments with yellow mercury oxide.* Similar experiments as above were undertaken on the yellow mercury oxide. The grid used for the experiments were made of lead antimony alloy plated with nickel as in the previous case. Four electrode plates were prepared having different constitution of the paste, which are shown in table 5.

Table 5.

Number of electrode plate	Amount of active material w (in gram)	Composition of paste		Weight of grid (in gram)
		Amount of Ag_2O mixed (in gram)	Amount of HgO mixed (in gram)	
1	5.26	4.50	1.50	16.95
2	5.00	4.00	4.00	15.37
3	4.81	2.00	6.00	15.10
4	5.68	—	10.00	15.70

When the paste was applied to the grids, each plate showed considerable stiffness, and seemed to give a satisfactory result. But in dipping in 20% KOH solution, the active materials of No. 3 and No. 4 have dropped off readily. The active material in No. 1 and No. 2 did not fall

Table 6.

Number of discharge n	Number of electrode plate			
	No. 1		No. 2	
	Discharge hour (in hours)	Discharge capacity C. (in ampere hours)	Discharge hour (in hours)	Discharge capacity C. (in ampere hours)
1	4.333	1.083	4.333	1.083
2	3.333	0.833	4.000	1.000
mean	3.833	0.954	4.167	1·042

off so much and could be formed into the positive electrode plate by the current of 100 milliamperes for about 96 hours. Immediately after the "formation," they were charged and discharged for two times.

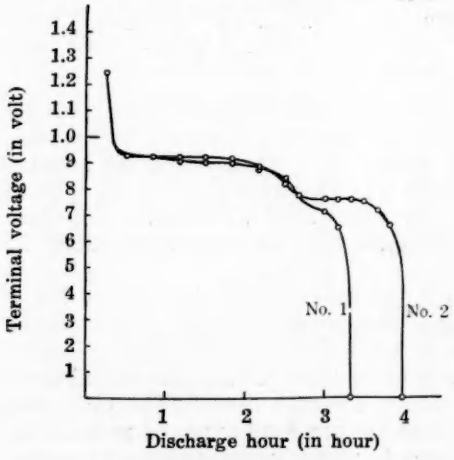

Fig. 4.

The colour of the plate of No. 1 was brown, when the paste was applied in the grids, and that of No. 4 yellow, and No. 2 and No. 3 showed medium colours between brown and yellow according to their constitution. The dischange current was taken to be 250 milliamperes and the charge was undertaken by the current of 200 milliamperes for about 10 hours. Table 6 shows the discharge capacity.

Fig. 4 shows the discharge characteristic curves.

Both No. 1 and No. 2 show the first stage of about 0.92 volt and the second stage of about 0.75 volt. This is just the same as obtained in the experiments with red mercury oxide. The fact that No. 2 which contains more mercury oxide than No. 1 has larger discharge capacity in the second stage, is the same tendency as seen in the red mercury oxide experiment.

(3) *Conclusion.* The positive plate of an accumulator in pasted form can be made by the mercury oxide (both red and yellow) provided that it is given some cohesive power as the active material by mixing with silver oxide.

The discharge characteristic curve has two steps in general, so that the whole discharge capacity can be divided into the two parts C_1 and C_2. The discharge characteristic curve of the first stage resembles much with the curve of the silver oxide positive plate, moreover, C_1 and C_2 stand in proportional relations with W_s and W_m, the quantities of silver oxide and mercury oxide in the active material respectively. This fact proves that C_1 is the result of the activity of silver oxide and C_2 the result of that of mercury oxide.

The appearance of the terminal voltage of about 1.2 volts at the beginning of the discharge, may be accounted for by the formation of silver peroxide. At present, the author will not discuss fully on the discharge characteristics of mercury oxide, but will insist the fact that if we can keep up mercury oxide as the active material of the electrode plate by some proper means, it can be used as the alkaline accumulator positive.

It was not possible to get an electrode plate made of yellow mercury oxide alone and the author can say nothing about it. In the case of red mercury oxide, however, the plate No. 6 which was made of red mercury oxide alone showed a small discharge capacity. This is a notable fact.

All these and the fact that the increasing of mercury oxide decreases the value of C_1/W_s seem to show the poor electrical conductivity of mercury oxide as the active material of electrode plate. It is thought to be probable from the result of experiments that the silver oxide mixed with the mercury oxide gives not only cohesive power but also better electrical conductivity of the active material, for it leaves powdered metallic silver as the result of the discharge.

Summary.

(1) Mercury oxide (both red and yellow) can be used into the electrode plate of the alkaline accumulator in the pasted form by mixing silver oxide.

(2) Its discharge characteristic curve varies in two stages, the first stage being caused by the discharge of silver oxide and the terminal voltage of about 0.95 volt. and the second stage being caused by mercury oxide.

(3) Mercury oxide seems to be a considerably poor substance in the electrical conductivity and the mixing of silver oxide raises its electrical conductivity.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his valuable advice.

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Zinc Content of the Hot Springs of Japan.

By **Kazuo KURODA.**

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Recently, considerable interest has been attached to the determination of the minute traces of rarer elements in natural waters and the observations have revealed the apparently universal distribution of heavy metals throughout the hydrosphere. A number of reports on the occurrence of zinc in sea water and in the mineral waters have already been published. The polarographic method for the determination of heavy metals such as copper, lead, nickel and zinc in the mineral waters has recently been quite well established by K. Heller, G. Kuhla and F. Machek.[1] P. R. Stout and his collaborators[2] have reported that the polarographic method is quite satisfactory for the determination of the minute traces of zinc in plant and animal tissues. The present author tested these methods and found that the following modified procedure was satisfactory for the determination of zinc in natural waters.

Method of Analysis. The method and apparatus used for the determination of zinc will be described in the following paragraphs.

(a) *Purification of the Diphenylthiocarbazone Carbon Tetrachloride Solution.* The solution of diphenylthiocarbazone in carbon tetrachloride was purified before use in the following manner:—Dissolve 0.1 g. of diphenylthiocarbazone in 100 ml. of carbon tetrachloride and wash the solution repeatedly with 6N hydrochloric acid in a separating funnel. Reject the aqueous layers, add 100 ml. of ammonia (5:95), shake, allow the layers to separate, reject the carbon tetrachloride layer. Add 100 ml. of carbon tetrachloride, acidify the aqueous layer with hydrochloric acid, draw off the carbon tetrachloride solution, and wash it with distilled water. This washed carbon tetrachloride solution constitutes the purified diphenylthiocarbazone reagent.

The amount of zinc derived from the glass bottle in which the mineral water was collected was found to be less than 10 γ per litre. The presence of zinc in water kept in the bottle for a long time was detected colori-

(1) *Mikrochemie*, **23** (1937), 78.
(2) *Collection Czechoslov. Chem. Commun.* **10** (1938), 129.

metrically, but it was difficult to estimate the amount by the polarographic method. The glass vessels was always washed with diphenylthiocarbazone solution before use to remove the traces of zinc and other heavy metals.

(b) *Extraction of Zinc with Diphenylthiocarbazone.* Add 10 ml. of N ammonium citrate solution to a suitable quantity (100 ml. to 500 ml.) of the mineral water, adjust to *p*H 8.5 with ammonia using phenol red as indicator, and shake with successive 10 ml. portions of the purified carbon tetrachloride solution of diphenylthiocarbazone. Continue the extraction until the carbon tetrachloride layer remains green. Wash the combined extracts with dil. ammonia (1:1000), run the carbon tetrachloride solution into a seperating funnel, and shake with three separate 10 ml. portions of 6N hydrochloric acid. Combine the acid layers and wash them by pouring small quantities of carbon tetrachloride through the aqueous liquid without shaking. Add 10 mg. of sodium chloride to the acid solution, and evaporate to complete dryness.

(c) *Determination of Zinc by the Polarographic Method.* Dissolve the residue in water, add 1 ml. of N ammonium acetate solution and 1 ml. of 0.25N potassium thiocyanate solution, and make up the volume of the solution to 10 ml. with water. A part of the solution is brought to a small electrolysis vessel, freed from the air by a current of hydrogen and then polarographically examined. The amount of zinc present is obtained from the height of the polarographic wave at −1.0 V. Fig. 1 shows a calibration curve obtained from various heights of wave due to various amounts of zinc salt in a solution which is 0.1N with respect to ammonium acetate and 0.25N to potassium thiocyanate, freed from atmospheric oxygen.

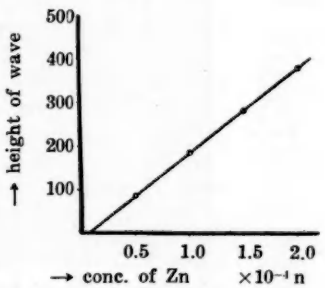

Fig. 1. The calibration curve for the wave due to zinc in a solution which is 0.1 N with respect to ammonium acetate and 0.025 N to potassium thiocyanate.

Results. The efficacy of the method was first tested by adding known amounts of standard zinc sulphate solution to 50 ml. of water and submitting the solutions to the complete process of extraction and polarographic examination; the results obtained are shown in Table 1.

Table 1.

Zinc added (γ)	Zinc found (γ)	Error (γ)
32.7	31.6	−1.1
65.3	67.1	+1.8
98.0	93.3	−4.7
130.6	136.9	+6.3

Further experiments were made in which known quantities of zinc were added to 1000 ml. of the mineral water, and submitted to the complete process of extraction. The results are given in Table 2.

Table 2.

No.	Mineral Waters	Zinc added to 1000 ml. of the mineral water (γ)	Zinc found (γ)	Difference (Zinc Content) (γ)
1	Monkawa, Kanagawa Prefecture	0	113	113
		65	176	111
2	Huezuka-Yu, Yunohanazawa, Kanagawa Prefecture.	0	20	20
		130	154	24
3	Drinking water of Yunohanazawa	0	46	46
		130	178	48

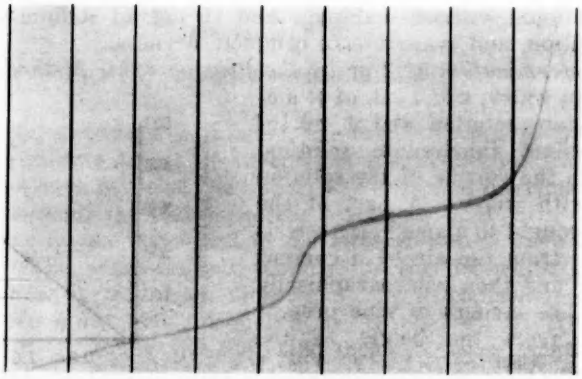

Fig. 2. Wave due to 68 γ of zinc extracted from the mineral water. (Military Sanatorium at the Misasa hot spring.) 0.1 N with respect to ammonium acetate and 0.025 N to potassium thiocyanate. Sensitivity $\frac{1}{10}$. Curve starts from zero E.M.F. 4 V. accummulator.

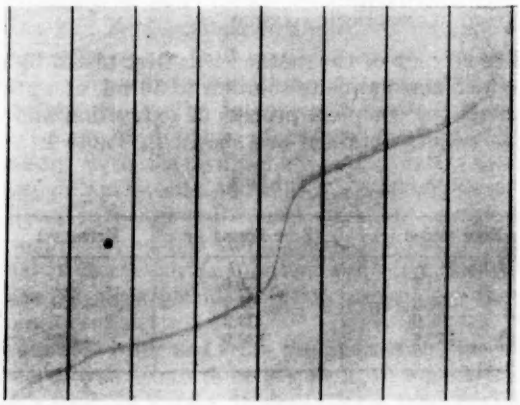

Fig. 3. Wave due to 112 γ of zinc extracted from the "Yuzawa No. 1" spring. 0.1 N with respect to ammonium acetate and 0.025 N to potassium thiocyanate. Sensitivity $\frac{1}{10}$. Curve starts from zero E.M.F. 4 V. accummulator.

The results of the determinations of the zinc contents, mainly of the hot springs of Japan, are collected in Table. 3.

Table 3.

Zinc Content of the Hot Springs of Japan.

No.	Hot Springs	Zinc Content.	
		(γ/l.)	% (total residue.)
(1)	Katakosi-Yu, Arima.	2010	0.0085
(2)	Yuzawa No. 10, Masutomi	284	0.019
(3)	Misasa Hotel, Misasa.	235	0.033
(4)	Yuzawa No. 1, Masutomi.	224	0.102
(5)	Kuridaira No. 1, Masutomi.	215	0.0060
(6)	Yuzawa No. 3, Masutomi.	164	0.082
(7)	Hana-no-Yu, Arima.	160	0.0009
(8)	Ikaho No. 1.	156	0.0014
(9)	Sanatorium at Misasa.	140	0.0045
(10)	Hon-Onsen. Arima.	140	0.0008
(11)	Military Sanatorium at Misasa.	136	0.0112
(12)	Yoemon-Yu, Yunohanazawa, Hakone.	132	0.0066
(13)	Yuzawa No. 5, Masutomi.	126	0.115
(14)	Daruma-Zigoku, Yunohanazawa.	120	0.0060
(15)	Wadamatuba, Masutomi.	113	0.0008
(16)	Monkawa.	113	0.0004
(17)	Yuzawa No. 4, Masutomi.	102	0.051
(18)	Yuzawa No. 7, Masutomi.	102	0.0065
(19)	Yagendo, Arima.	96	0.0009
(20)	Yuzawa No. 2, Masutomi.	88	0.0151
(21)	Sanatorium of the Medical College of Okayama at Misasa.	81	0.0053
(22)	Yuzawa No. 6, Masutomi.	80	0.022
(23)	Kinsentō, Masutomi.	80	0.0011
(24)	Ginsentō, (Huru-Yu), Masutomi.	80	0.0078
(25)	Ginsentō (Naka-no-Yu), Masutomi.	78	0.0080
(26)	Nanasigure.	73	0.0006
(27)	Bansuiro, Misasa.	66	0.0042
(28)	Yuzawa No. 9, Masutomi.	64	0.0042
(29)	Wadegawara (Simo-no-Yu), Masutomi.	64	0.0009
(30)	Yuzawa No. 8, Masutomi.	60	0.0036
(31)	Aziro.	46	0.0004
(32)	Higasiobi, Masutomi.	39	0.0004
(33)	Gantōhunsen, Masutomi.	35	0.0012
(34)	Kōbō-Yu, Yunohanazawa.	34	0.0034
(35)	Tuganerō, Masutomi.	26	0.0003
(36)	Umamitizawa, Masutomi.	26	0.0007
(37)	Gongen-Yu, Yunohanazawa.	25	0.0039
(38)	Huezuka-Yu, Yunohanazawa.	20	0.0033
(39)	Hii-no-Yu, Matunoyama.	less than 10	0.000
(40)	Tamagono-Yu, Matunoyama.	less than 10	0.000
(41)	Iriyamabe.	less than 10	0.000
(42)	Simokurohira,	less than 10	0.000
(43)	Hiukemizu, Masutomi.	less than 10	0.000
(44)	River water, Yunohanazawa.	less than 10	0.000
(45)	Sea water, Yosihama.	less than 10	0.000
(46)	Drinking water of Yunohanazawa.	46	0.0170
(47)	Tap water of Tokyo, Oct. 26, 1939.	116	
(48)	Tap water of Tokyo, Oct. 27, 1939.	133	
(49)	Tap water of New York.	124	
(50)	Distilled water.	less than 10	

Table 3. shows that the traces of zinc are widely distributed in the mineral waters in Japan. The mineral springs of Arima had the highest

zinc content. The average zinc content of forty-three samples was 0.013% (of the total residue), or 136 γ per litre. The presence of zinc in sea water was detected colorimetrically, but the author could not estimate the amount polarographically. The zinc content of sea water is considered to be less than 10 γ per litre.

Summary.

(1) The polarographic method was tested and found to be satisfactory for the determination of zinc in natural waters.

(2) The zinc content of a number of hot springs of Japan was polarographically estimated.

(3) The amount of zinc in sea water is considered to be less than 10 γ per litre.

The author wishes to express his hearty thanks to Prof. Kenjiro Kimura for his kind guidance. It is author's pleasant duty to acknowledge the valuable advice offered by Dr. H. Hamaguti. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by The Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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Studies on the Organic Molecular Compounds. Part I. The Influence of Nitro Radicals and Second Substitution Radicals on the Formation of the Aromatic-Nitroaromatic Molecular Compounds. I.

By Chiro SHINOMIYA.

(Received February 5, 1940).

Graduation of Molecular Compound Formation. Organic "molecular compound formation" is discussed in this paper, with the binary solid—liquid phase equilibrium diagram as basis. The aromatic—nitroaromatic molecular compound formation studied by the writer is summarised schematically in Fig. 1.

Curve $A_1C_1B_1$ indicates a stable compound type with a congruent melting point C_1. Curves A_1DB_2, A_2UB_1, and $A_2E_eB_2$ in the diagrams illustrate the successive changes that occur with the decrease of the tendency of compound formation.(1) A_1DB_2 is a dissociation type,

(1) For simplicity, only a single compound of the type AB (1 : 1) is considered. The argument, however, can readily be extended to other types.

A_2UB_1 an incongruent type, and $A_2E_6B_2$ a simple eutectic type, for which last named no compound is found in the diagram.

The Existence Range of Molecular Compounds. In the ideal case, the crystallisation curve A_2E_6 represents the ideal solution equation, namely

$$\ln x = -\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where x is the mol fraction of A_2 in the saturated solution at temperature T, Q the differential mol heat of solution of A_2, T_0 the melting point of pure A_2, and R the gas constant. Curve B_2E_6 is also of a similar nature. E_6, the intersection of the two curves, is the eutectic point of this system.

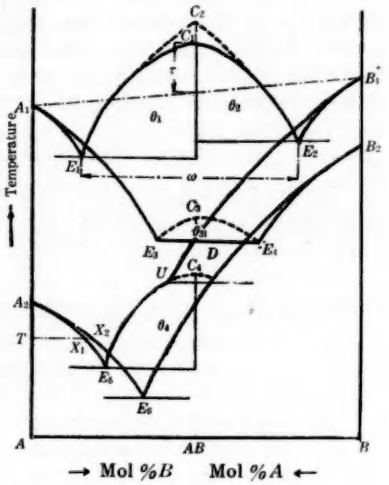


Fig. 1.

Kendall and his co-workers,[2] who studied the various factors that induce deviations from the ideal solubility curve in polar systems, concluded that the predominant disturbing factor is the "addition compound formation" between the components of the systems. The essential point to be noted is the depression of the crystallisation curve (AE or BE) from its ideal position, which is made necessary by compound formation in the solution.[3]

"If only a part of the total A in solution exists as uncombined A, then the total mol fraction of A in the saturated solution must exceed the ideal value by an amount depending on the stability of the compound AB in the liquid state, since the solution will not become saturated with respect to A until the mol fraction of uncombined A reaches this ideal value." Consequently, in Fig. 1, at any fixed temperature T under the melting point of A_2, the solubility of A_2 in the system A_2UB_1 is larger than that in $A_2E_6B_2$, as also the solubility of A_1 in the system $A_1C_1B_1$ is larger than that in A_1DB_2.

Increasing solubility and increasing tendency of compound formation, therefore, for one fixed component (A_1) in a series of different anothers (B_1 or B_2, etc.), proceed in parallel. Since it is the same when we take B in place of A, the increased solubility necessitates an enlarged range of existence of compounds ($E_1E_2 = \omega$ in the system $A_1C_1B_1$) in the solid—liquid equilibrium state.

(2) J. Kendall, A. W. Davidson, H. Adler, *J. Am. Chem. Soc.* **43** (1921), 1481.

(3) Curve A_2E_6 is asymptotic to the ordinate at B ($x = 0$), and curve A_1E_1 is asymptotic to the ordinate at AB ($x = 0.5$). In the remaining case, AE assumes an intermediate position between the two.

The Melting Point of Molecular Compounds[4]. Increasing stability of the compound and elevation of its melting point also proceeded in parallel. In the system $A_1C_1B_1$, the virtual point C_2 indicates the melting point of the compound, not dissociated into its components in the fused state, the system consisting, indeed, of two simple eutectic systems of type $A_2E_6B_2$ compressed into one composition range. Point C_1 is the dystectic point of an actual compound in which some degree of dissociation is realized on fusion,

$$AB \rightleftarrows A+B.$$

In the less stable A_1DB_2 system, further dissociation takes place, the crystallisation curve $E_3C_3E_4$ becomes flatter, and, finally, in the case of complete dissociation, it coincides with the straight line E_3DE_4.

Generallization is used here in order to compare the compound formation in systems of various types. It has been shown that—

(a) Compound formation and its stability decreases in the order,[5] congruent type $>$ dissociation type, incongruent type $>$ simple eutectic type.

(b) In the first three types, where compound crystals are perceived, the order of compound formation is generally parallel to the solubility of the mutual components, which spreads the existence range of the compound: ω.[6]

(c) In the congruent melting type, stability is related to the curvature of the crystallisation curve near the dystectic point.

In the non-dissociation type, the dystectic point C_2, which designates the melting point of a pure solid compound, is on the apex of $E_1C_2E_2$, although usually in the case of organic molecular compounds in the fused state, dissociation takes place to a certain extent, so that, the crystallisation curve becomes progressively flat with the depression of the melting point, whence the greater the dissociation, the lower the melting point.

Regardless of this consideration, actually, the melting point of the molecular compound is higher or lower than that of the component, depending on other intermolecular factors. At present, these factors are so complicated that no satisfactory resolution has yet been accomplished. However, if we take the following value τ from a large number of congruent systems, consisting of analogously constituted components, we can conveniently compare the sequence of compound formation, namely,

$$\tau = t_c - \frac{mt_A + nt_B}{m+n},$$

where t_A, t_B, and t_C are respectively the melting points of the binary components and their compound, $m:n$ is the compound mol ratio ($A:B = m:n$), and τ is provisionally called the "melting point elevation."

(4) R. Kremann, *Monatsh.*, **25** (1904), 1215; *Z. Elektrochem.*, **12** (1906), 259.
(5) Crystallisation velocity is greatly diminished in viscous liquids.
(6) Area θ in Fig. 1 may be taken for this comparison.

The Molecular Compounds between Naphthalene, Naphthols, and Aromatic Nitrobenzenes[7]. In recent crystal chemistry, the crystal lattices of typical organic compounds have gradually been found to belong to the molecular lattice type. Benzene,[8] naphthalene,[9] anthracene,[9] and the series of the aromatic condensed ring compounds with simple substitution radical[10] have been determined as having ~~the~~ flat molecular structure. Fixation of the lattices by intermolecular force is generally weakened by melting. At the melting point, the crystal lattice structure being disturbed, a freer molcular state follows, in which the molecular compounds usually dissociate into their components. In this sense, it is possible to discuss the formation and stability of molecular compounds in fusion together with the structure of their components. Tables 1 and 2[7] give the essential data of molecular compounds between naphthalene, naphthols, and aromatic nitrobenzenes.

Table 1. Binary Systems of Trinitro and Tetranitro Compounds.

Mol ratio A : B (ω) A / B	α-Naphthol	β-Naphthol	Naphthalene
sym-Trintrobenzene	1 : 1 (84.0) 90·6	1 : 1 (36.0) 76·7	1 : 1 (51.0)* 83·4
Picric acid	1 : 1 (81.5) 92·8	1 : 1 (34.3)** 78·7	1 : 1 (50.5)* 86·4
Picramide	1 : 1 (52.3) 71·3	1 : 1 (7.3) 56·0	1 : 1 (34.8)* –
2, 4, 6-Trinitrotoluene	1 : 1 (37.8) or (3 : 2) 73·2	1 : 1 (8.3)* –	1 : 1 (17.3)* 72·7
Picryl chloride	1 : 1 (34.5) 71·9	1 : 1 (3.5) 52·3	1 : 1 (10.5)* –
2, 4, 6-Trinitroanisol	1 : 1 (−4.0) 49·0	∨	∨ or 1 : 1 (−20.0) 22·3
2, 4, 6-Trinitrophenetol	1 : 2 (−16.0) 32·3	1 : 2 (−17.2) 29·4	1 : 2 (−5.7) 45·1
Trinitrocresol	1 : 1 (58.8) or (3 : 2) 91·0	1 : 1 (15.3) 66·9	1 : 1 (32.8)* 87·2
Styphnic acid	1 : 1 U* –	1 : 1 U* –	2 : 1 (26.0) or (1 : 1)* 17·5
1, 2, 4, 6-Tetranitrobenzene	1 : 1 (26.0) 73·5	1 : 1 (6.5) 64·6	3 : 2 (41.1) 84·7
Tetryl	3 : 2 (−29.0) 19·7	m : n (−46.3) D –	1 : 1 (−17.5)* –

* Landolt, Börnstein, "Physikalisch-chemische Tabellen", 5 Aufl., **122**.
** Asahina, Yokoyama, *J. Chem Soc. Japan*, **56** (1925), 415.

(7) T. Asahina and C. Shinomiya, *J. Chem. Soc. Japan*, **59** (1938), 341; C. Shinomiya, *J. Chem. Soc. Japan*, **59** (1938), 833, 922; **60** (1939), 170.
(8) E. G. Cox, *Proc. Roy. Soc.* (London), A, **135** (1932), 491.
(9) J. M. Robertson, *Proc. Roy. Soc.* (London), A, **142** (1933), 674; **140** (1933), 79.
(10) R. C. Evans, "An Introduction to Crystal Chemistry", 335–349, Cambridge (1939).

Table 2. Binary Systems of Dinitro and Mononitro[11] Compounds.

Mol ratio A : B (-) / B	α-Naphthol	β-Naphthol	Naphthalene
2, 4-Dinitrobenzoic acid	1 : 1 U	1 : 2 U or ∨	1 : 1 U
2, 4-Dinitrochlorobenzene	1 : 1 (35.7)	1 : 1 (6.7)	1 : 1 (13.2)
2, 4-Dinitrophenol	1 : 1 (14.7)	1 : 1 (−8.3)	1 : 1 (−4.0)
2, 4-Dinitrobromobenzene	1 : 1 (12.3)***	1 : 1 (−15.7)***	1 : 1 (−5.7)***
2, 4-Dinitrotoluene	1 : 1 (15.0)	1 : 1 (−19.5)	1 : 1 (−14.5)
m-Dinitrobenzene	1 : 1 (7.0)	1 : 1 U*	1 : 1 (−34.2) D*
2, 4-Dinitroanisol	1 : 1 (2.0)	1 : 1 (−22.0)	1 : 1 (−33.5)
2, 4-Dinitroaniline	1 : 1 (2 : 3) or U	2 : 3 U	1 : 3 U
Dinitromesitylene	∨	∨	∨
2, 6-Dinitrophenol	1 : 1 (0.8)	1 : 1 (−16.7)	1 : 1 (−13.8)
2, 6-Dinitrotoluene	1 : 1 U	∨	∨*
2, 6-Dinitroaniline	1 : 1 U	1 : 1 (12.0)	1 : 1 U
3, 5-Dinitrobenzoic acid	1 : 1 (41.5)	1 : 1 (22.0)	1 : 1 (39.5)
3, 5-Dinitroanisol	1 : 1 (−7.3	∨	1 : 1 U
2, 5-Dinitrophenol	1 : 1 (17.4)	1 : 1 (3.4)	3 : 2 (10.1) or (1 : 1
2, 5-Dinitrotoluene	1 : 1 (11.9)	1 : 1 (−8.5)	1 : 1 (−19.6)
p-Dinitrobenzene	1 : 1 U	1 : 1 (−11.8) or (3 : 2)	1 : 1 (−7.5)*
p-Nitrobenzoic acid	1 : 1 U	1 : 2 U	1 : 1 U
m- ,,	1 : 2 (3.3)	∨ or 1 : 1 (−24.3)	1 : 2 (10.2)
o- ,,	∨	∨	∨
p-Nitrobenzaldehyde	3 : 2 (−21.6)	1 : 1 (−37.0)*	∨
m- ,,	1 : 1 (−29.0)	1 : 1 U*	∨
o- ,,	1 : 1 U	∨*	∨
p-Nitrochlorobenzene	2 : 3 (−37.0)	∨	∨
m- ,,	∨	∨	∨
p-Nitrophenol	∨	∨	∨*
m- ,,	∨	∨	∨
o- ,,	∨	∨	∨*
p- or *m*-Bromobenzene	∨	∨	∨
p-Nitrotoluene	∨	∨	∨*
m- ,,	—	—	∨*
Nitrobenzene	—	—	∨*
p-Nitroaniline	∨	∨	∨
m- ,,	∨	∨	∨*
o- ,,	∨	∨	∨
p-Nitroanisol	∨	∨	∨

* Landolt, Börnstein, "Physikalisch-chemische Tabellen", 5 Aufl., **122**.

*** Data of the molecular compound obtained from the solution by Buehler, Hisey, Wood (*J. Am. Chem. Soc.*, **52** (1930), 1940.).

(11) Some of the liquidus in systems of simple eutectic type are in fairly good agreement with their ideal crystallisation curves.

(1) Compound ratio usually 1:1, except the following systems:

3 : 2 naphthalene — 1,2,4,6-tetranitrobenzene, α-naphthol — tetryl, naphthalene—2,5-dinitrophenol, α-naphthol — p-nitrobenzaldehyde;

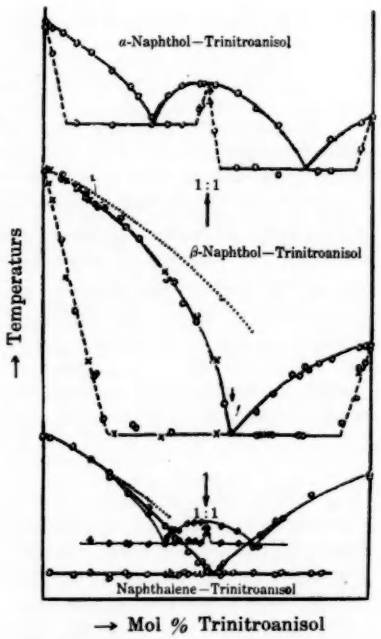
2 : 3 naphthol—2,4-dinitroaniline, α-naphthol—p-nitrochlorobenzene;

1 : 2 naphthol — 2,4,6-trinitrophenetol, naphthalene — 2,4,6-trinitrophenetol, β-naphthol — 2,4-dinitrobenzoic acid, β-naphthol — p nitrobenzoic acid, α-naphthol—m-nitrobenzoic acid, naphthalene —m-nitrobenzoic acid;

1 : 3 naphthalene—2,4-dinitroaniline.

Except a few examples, ratios other than 1:1 are found in the case of rather feeble compound formations, in which case there sometimes happens to be another metastable equilibrium, the molecular ratio of which is given in Tables 1, 2 in parentheses.

(2) From Tables 1, 2, which are arranged in the order of decreasing tendency of compound formation, it will readily be seen by comparing the value of τ or ω that compounds of α-naphthol have higher "melting



○ Stable thawing and melting point.

× Date from the measurement by the cooling method.

◆ Metastable point.

△ Transition point of the crystal obtained in the alcoholic solution.

··· Ideal crystallisation curve calculated from the equation

$$\ln x = -\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where Q is 5.4 or 4.6 kg. cal. respectively in β-naphthol or naphthalene.

Fig. 2.

point elevation" and a wider compound existence range than those of β-isomer (the only exception being β-naphthol—2,6-dinitroaniline). Most of the naphthalene compounds have intermediate values of τ or ω.

It is interesting to compare, of the various feeble compound formation systems, α-naphthol compound with a β-isomer or naphthalene compound. Trinitroanisol which gives a compound of congruent melting point with α-naphthol, fails to give one with β-naphthol, while it gives with naphthalene a simple eutectic or a metastable compound. Analogous examples are to be seen in the compounds of *m*-nitrobenzoic acid.

In *m*-nitrobenzene, 2,4-dinitroaniline, 2-6-dinitrotoluene, 3,5-dinitroanisol, and *p*-, *m*- and *o*-nitrobenzaldehydes, the orders of compound formation are clearly systematized.[12]

(3) In comparing the columns of Tables 1 and 2, the order of compound formation is readily seen to be

trinitro compound $>$ dinitro compound $>$ mononitro compound,

and the effect of second substitution radical in the nitrated benzene nucleus,

sym-Trinitro compounds: $-H > OH > NH_2 > CH_3 > Cl > OCH_3$, OC_2H_5,

2,4-Dinitro compounds: $-CO_2H > Cl > OH > Br > CH_3 > H > OCH_3 > NH_2$,

Mononitro compounds: $-CO_2H$, $CHO > Cl > Br$ - - - .

The tendency of compound formation is the most marked in symtrinitrobenzene, the substitution of any other radicals into it diminishes the tendency, presumably because of certain hindrances. In the case of less nitrated compounds, the effect of the substituent is profound, whether positive or negative. Of the molecular compounds of mononitrobenzenes, those of naphthalene somewhat differ in nature from those of naphthols.

(4) A comparison of isomers of equally nitrated components also gives a number of interesting results in connection with the affinity of molecular compounds. In di- and mono-nitrobenzenes, the orders are,

p-nitro compound, *m*-nitro compound $>$ *o*-nitro compound;
2, 4-dinitro compound, 2, 5-dinitro compound, 3, 5-dinitro compound $>$ 2, 6-dinitro compound.

More detailed results will be given in a later paper.

(5) These compounds[13] showed distinctly halochromic phenomenon, and naphthols were more coloured than naphthalene, owing probably to the presence of the hydroxyl group. Between α- and β-naphthol, most of the α-compounds proved to be more halochromic than the β-isomers.

These molecular compound crystals were prepared from the solution, and most of them showed melting points identical with those obtained in the phase diagrams.

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(12) Incongruent melting point was found not only in feeble combinations but also in systems, one component of which had a much higher melting point than the other.

(13) P. Pfeiffer, "Organische Molekulverbindungen", 2. Aufl., 338, Stuttgart (1927).

Experimental.

Determination of Solid-Liquid Transion Points. The phase diagram was obtained by improving the thawing and melting point method of H. Reinboldt [14], by which the least quantity of sample (10–100 mg.) could be investigated in a short time.

The apparatus consisted of the following parts.

(a) A thermometer of very small diameter. A rod thermometer about 150 mm. long, 2–3 mm. diameter, with a mercury bulb of the same diameter 2–3 mm. long. Accurary of temperature reading about 0.2°.

(b) Sample tube. The glass tube shown in Fig. 3. The upper stem was made exactly to fit the thermometer inserted in it, in order to prevent the inner wall of the lower bulge from touching the sample throughout the observation.

(c) Heating vessel (not illustrated). To regulate the heating, an air mantle was adopted and immersed in a liquid bath for which liquid paraffin or concentrated sulphric acid was found to be convenient. The bath was provided with a thermometer and a stirrer.

(d) Weighing. To save time, the sample could be weighed with a torsion or a micro spring balance (0.1–100 mg.). The present writer used a quartz spring balance that is a modification of Salvioni's microchemical balance.

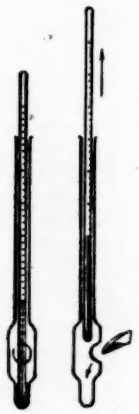

Fig. 3.

The weighed sample was placed through a side hole in the sample tube, and the thermometer introduced. The substance was fused to a homogeneous mixture. After cooling, the sample tube containing the solidified substance was placed in the liquid bath, heated gradually and constantly, and the thawing point observed. The thawed sample was then further heated with a little stirring with the thermometer until it completely melted, when the melting point was observed. (Both thawing and melting point can be frequently observed, their values being usually the same.) Supercooling was avoided by rubbing or crystal seeding, which made it possible to obtain a detailed curve near the eutectic point [15]. The observation was repeated by varying the composition, which was effected by slightly drawing up the thermometer (as in Fig. 3b) and adding one component to the mixture.

The capillary tube method [16] was also used in experimenting with readily sublimable or decomposable material. Some of the data obtained by the cooling curve method are included in the above mentioned tables.

Preparation of the Molecular Compound from the Solution. In the system, the molecular compound formation of which was observed in the diagram, the writer tried to obtain a crystal of the compound from the solution containing its components. From 0.1 to 0.2 g. of the components was weighed in a compound ratio, separately dissolved in alcohol, and the warmed solutions were mixed together, the mixture which, after a short heating, was slowly poured into 50–100 cc. of distilled water with vigorous stirring. The separated crystal was suctioned, washed with distilled water (if permitted), pressed between sheets of filter paper, and dried overnight in a desiccator. The yield of products seems to agree with the compound formation in the diagram.

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(14) H. Reinboldt, K. Henning and M. Kircheisen, *J. prakt. Chem.*, [2], **111** (1925), 246; C. Shinomiya, *J. Chem. Soc. Japan*, **58** (1937), 118.

(15) Supercooling is very frequent near the eutectic composition, in which case, supercooled viscous liquid was easily made to crystallise when some crystals of that component (not the other), which should give heterogeneous equilibrium with the liquid, were seeded. In this way, it is easy to determine whether the composition of the mixture lies on the A-component side or on the B-component side of the eutectic composition.

(16) A method devised and modified from the original by T. Asahina. (*Bull. Chem. Soc. Japan*, **9** (1934), 132.)

Special Part.

(1) α- or β-Naphthol—1,2,4,6-tetranitrobenzene.

These system are too unstable to enable a determination of diagrams.

With α-naphthol,

Eutectic point: 74.0°, 111.0°; 87 mol%, 13.5 mol% α-naphthol.
Compound (1:): brown red prisms. melting at 137.0°.

with β-naphthol,

Eutectic point: 95.0°, 110.0°; 82.6 mol%, 18 mol% β-naphthol.
Compound (1:1): brown red powder, melting at 130.5°.

(2) Naphthalene—1,2,4,6-tetranitrobeneze.

Tetranitrobenzene: 5.0 mg.

Mol% tetranitrobenzene	100.0	75.5	59.4	42.9	33.6	19.0	9.2
Melting point	126.0	128.0	135.0	138.0	138.0	129.0	92.0
Thawing point	125.0	—	111.0	129.0	—	73.0	73.0

Tetranitrobenzene: 7.6 mg.

Mol% tetranitrobenzene	88.4	67.7	49.2	34.7	24.1	18.1	12.5	6.4[17]	4.7
Melting point	119.0	132.0	138.0	139.0	—	—	116.5	75.0 ↓	74.0
Thawing point	114.0	114.0	—	108.0	75.0	74.0	74.0	74.0 ↓	76.5

Total naphthalene: 21.0 mg.

Mol% naphthalene	80.0	74.0	58.5	48.9	43.0	35.6	28.3
Melting point	—	—	139.5	138.0	139.0	139.0	—
Thawing point	74.0	74.0	134.0	114.0	114.0	120.0	74.0

Eutectic point: 74.0°, 114.0°; 93.7 mol%, 9 mol% naphthalene.
Compound (3:2): orange yellow prism melting at 139.5°.

This system was the most stable of the three, whereas with trinitro or dinitro compounds, α-naphthol usually formed the most stable compound. In Fig. 4, however, the curvature near the melting point is extreamely flat, and considerable dissociation is expected.

The conclusion is that tetranitrobenzene is not a stable substance [18], its tendency of molecular compound formation with naphthalene and naphthols is not so marked as that with *sym*-trinitrobenzene.

(3) α-Naphthol—tetryl (Fig. 5).

Naphthol: 6.7 mg.

Mol% naphthol	95.7	88.1	75.6	69.8	59.0	44.0	34.3	27.0
Melting point	93.0	88.5	79.0	77.5	80.0	97.5	106.0	116.0
Thawing point	84.0	76.0	75.5	75.0	78.0	78.0	78.0	77.0

Tetryl: 7.1 mg.

Mol% tetryl	94.6	54.4	49.1	43.1	39.8	34.7	27.3	17.5	6.5
Melting point	126.0	90.0	83.0	80.0	80.0	79.5	76.0	85.5	92.3
Thawing point	117.0	77.0	77.0	77.0	—	77.0	75.0	75.0	76.0

Naphthol: 12.0 mg.

Mol% naphthol	75.4 ↓	66.9	61.3	57.5 ↓	52.7	50.4
Melting point	79.0 ↓	79.0	80.0	80.0 ↓	79.5	85.5
Thawing point	76.0 ↓	75.5	78.0	78.5 ↓	77.0	77.6

Eutectic point: 75.5°, 77.0°; 72.6 mol%, 52.9 mol% α-naphthol.
Compound (3:2): brown red prisms, melting at 80.0°.

(17) In the sample of 6.4 moles% tetranitrobenzene, its molecular compound crystal was recognized, while in that of 4.7 moles% tetranitrobenzene, naphthalene was seen in the last stage of melting. The arrow indicates the position of the eutectic point.

(18) 1, 2, 4, 6-Tetranitrobenzene was easily prepared by the method of W. Borsche (*Ber.* **56** (1923), 1939.). Instead of trinitrophenetol in alcoholic solution, trinitroanisol in methyl alcohol was used. The crude picryl hydroxylamine immediately nitrated, tetranitrobenzene was formed, which was decomposed considerably by repeated crystallisations in chloroform.

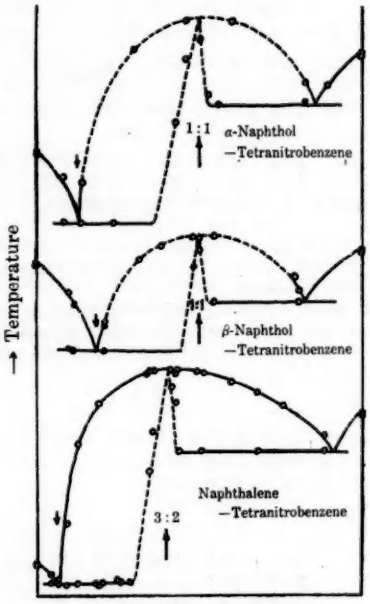

Fig. 4.

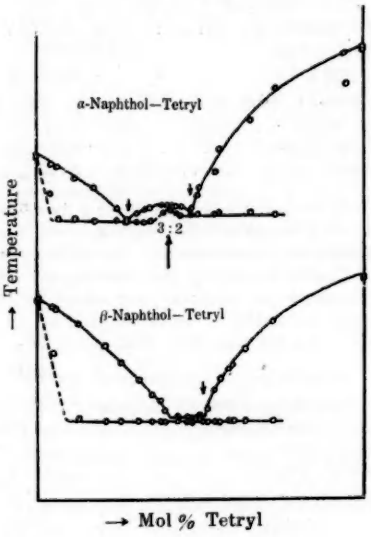

Fig. 5.

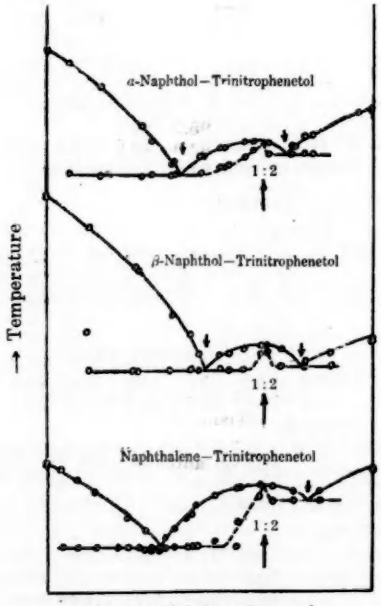

Fig. 6.

(4) β-Naphthol—tetryl (Fig. 5).

Total naphthol: 9.4 mg.

Mol% naphthol	94.5	79.9	87.8	74.8	65.2	54.1	50.6	46.2	40.6	27.9
Melting point	11.85	107.0	114.0	102.0	92.0	85.5	86.0	94.0	101.0	114.5
Thawing point	—	84.0	85.0	84.5	84.0	84.0	85.0	83.8	84.0	84.0

Tetryl: 17.2 mg.

Mol% tetryl	95.9	69.1	62.4	61.7	57.2	53.3	48.4	44.6	41.5	36.9
Melting point	119.0	97.0	90.5	87.0	86.0	85.0	88.0	97.0	100.0	106.0
Thawing point	105.0	84.0	84.0	84.0	84.0	84.0	84.0	83.8	83.8	84.0

This last mentioned system is of dissociation type. In the range of 59.6–49.6 mol% of β-naphthol, the melting curve was a straight line. The compound ratio was indistinct although brownish halochromy was very marked.

Notwithstanding the abundance of nitro groups, two tetranitro compounds have never shown any notable compound formation, probably owing to steric hindrances or ortho nitro effect. In these systems, it is noteworthy that the addition of naphthalene is more marked than that of the two naphthols.

(5) α-Naphthol—2,4,6-trinitrophenetol.

Trinitrophenetol: 5.0 mg.

Mol% trinitrophenetol	100.0	75.6	32.2	16.8	7.0
Melting point	78.0	66.0	68.0	84.8	92.0
Thawing point	77.0	—	57.5	57.8	58.0

Naphthol: 3.2 mg.

Mol% naphthol	60.5	51.3	43.8	35.2	31.8	18.0
Melting point	62.0	63.5	—	67.0	66.8	70.0
Thawing point	58.0	—	60.8	65.0	63.0	64.0

Total trinitrophenetol: 16.3 mg.

Mol% trinitrophenetol	96.0	63.8	55.0	60.9	53.7	47.3	38.5	29.3
Melting point	76.5	67.8	66.3	67.8	65.5	63.3	61.0	73.0
Thawing point	—	65.0	60.0	63.0	60.0	58.0	57.8	57.0

Naphthol: 1.5 mg.

Mol% naphthol	24.5	20.8
Melting point	67.0	70.0
Thawing point	64.3	64.0

Eutectic point: 57.5°, 64.0°; 58.3 mol%, 26.0 mol% α-naphthol.
Compound (1:2): orange prisms or powder, melting at 68.0°.

(6) β-Naphthol—2, 4, 6-trinitrophenetol.

Total trinitrophenetol: 9.3 mg.

Mol% trinitrophenetol	83.4	53.0	67.0	44.2	28.3
Melting point	71.5	73.0	75.0	79.5	99.5
Thawing point	—	68.5	73.0	69.0	68.0

Naphthol: 4.2 mg.

Mol% naphthol	87.2	72.4	61.6	53.1	44.7	39.8	34.5	27.8	20.8	12.8
Melting point	112.0	100.0	85.0	73.0	73.0	74.0	75.5	74.5	71.0	73.3
Thawing point	68.0 (80.0)	68.0	68.0	68.0	68.0	68.0	73.0	69.0	69.0	69.0

Eutectic point: 68.0°, 69.0°; 51.1 mol%, 21.7 mol% β-naphthol.
Compound (1:2): orange yellow prisms or powder, melting at 75.5°.

(7) Naphthalene—2,4,6-trinitrophenetol.

Trinitrophenetol: 6.3 mg.

Mol% trinitrophenetol	58.8	34.8	24.4	15.8	9.3	4.3
Melting point	72.0	54.0	63.0	—	75.0	78.0
Thawing point	62.0 (54.0)	53.0	54.0	54.0	54.0	54.0

Trinitrophenetol: 13.1 mg.

Mol% trinitrophenetol	83.4	75.7	69.3	65.2	59.3	51.8	46.0		
Melting point	71.0	71.0	72.8	73.0	72.0	70.0	67.0		
Thawing point	68.0	68.0	68.0	69.5	—	56.0	54.0		

Trinitrophenetol: 3.1 mg. [19]

Mol% trinitrophenetol	44.5	42.9	39.1	36.3	34.1	29.9	28.1	21.4	14.3
Melting point	64.0	63.0	60.0	57.0	—	59.0	—	64.0	71.0
Thawing point	54.0	54.0	54.0	54.0	54.0	53.0	54.0	54.0	54.0

Eutectic point: 54.0°, 68.0°; 64.9 mol%, 19.8 mol% naphthalene.
Compound (1:2): pale yellow powder or prisms, melting at 73.0°.

Three diagrams of trinitrophenetol are given in Fig. 6. The order of compound formation is naphthalene > α-naphthol > β-naphthol. It is related in character to tetranitro compounds, rather than to trinitroanisol. Substitution of ethyl by a methyl radical somewhat affects addition compound formation.

Summary.

The molecular compound of naphthalene and naphthols with mono-, di-, tri-, and tetra-nitro aromatic compounds are systematically compared, and the compound formation discussed with solid—liquid phase diagrams.

In conclusion, the writer wishes to express his sincere thanks to Prof. B. Kubota of the Tokyo Imperial University for his kind guidance and encouragement throughout this study and to Dr. T. Asahina for much valuable advice. Thanks are also due to the Hattori-Hokakai for a grant, with which the expenses connected with the study have been defrayed, and to Mr. R. Takagi for his gift of materials.

— See Correction in No. 12 p. 690

Chemical Institute, Faculty of Science,
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and
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On the Action of Phosphate upon Hexoses. IV. Formation of Lactic Aldehyde side by side with Acetol.

By Ryozo GOTO.

(Received February 9, 1940).

In the previous papers[1] of this series, it has been reported that when a mixture of glucose and a slightly acidic (*p*H 7-5) concentrated solution of potassium phosphate (about 40%) was distilled, acetol was

(19) This datum, together with the value of the cooling method in Fig. 2, is due to Mr. N. Sato, whom the writer wishes to thank for his assistance.

(1) R. Nodzu and his co-workers, this Bulletin, **10** (1935), 122; 467; *Mem. Coll. Sci. Kyoto Imp. Univ.*, **20** (1937), 197.

found in the distillate, accompanied by small quantities of methylglyoxal, diacetyl and some indistinct substances, and that pyruvic acid was present in the distillation residue. From these facts, we have postulated that under these conditions glucose molecule may split into acetol and pyruvic acid, as well as into others.

In the present work, the same distillation experiment was repeated with a larger amount of the materials and the distillate was studied more thoroughly. Besides acetol and the other products described above, the presence of lactic aldehyde and of pyruvic acid was confirmed. At first sight, the appearance of lactic aldehyde side by side with acetol was somewhat surprising, since it has long been known[2] that the former transforms very easily into the latter. It was found, however, that by the same distillation process, not only lactic aldehyde did convert almost completely into acetol, but the reverse process also took place and a small portion of the acetol changed into lactic aldehyde. Hence, at least in the solution of phosphate, both substances seem to be in a relation of desmotropic equilibrium:

$$\underset{\text{Acetol}}{CH_3COCH_2OH} \rightleftarrows \underset{\text{Lactic aldehyde}}{CH_3CHOHCHO}$$

shifting far on the left hand side. It is accordingly indecisive which of the two is the precursor in the postulated scheme of cleavage of glucose molecule:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{-H_2O} \underset{\text{(Acetol or Lactic Aldehyde)}}{C_3H_6O_2} + \underset{\text{Pyruvic acid}}{CH_3COCOOH}$$

Experimental Part.

Glucose. The distillate[3] (about 9 litres, about 5g. acetol) obtained from a mixture of 200g. glucose and 2 litres of 40% potassium phosphate solution (*p*H 5,2–5,6), was warmed on a boiling water bath for about half an hour with enough semicarbazide hydrochloride and sodium acetate to equal eight equivalents of the acetol content, was left to stand over night, and then filtered. The filtrate was evaporated[4] to about 500 c.c. under a reduced pressure of carbon dioxide. After filtering off a yellowish white precipitate, the filtrate was concentrated further until an appreciable amount of precipitate reappeared and then filtered again. Repeating this process several times, four kinds of precipitates tabulated were obtained.

	m.p.	g.
I.	258°	0.7
II.	195°	4.8
III.	190°	2.35
IV.	239°	0.17

(2) Nef (*Ann.*, **335** (1904), 247.) has suggested that "Das Acetol ist mit Oxyaceton identisch; der isomere *r*-Milchsäurealdehyd, *r*-$CH_3CHOHCHO$, existirt nicht, sondern geht in Acetol über." A. Wohl, *Ber.*, **41** (1908), 3599.

(3) The distillation, and the estimation of the iodine-consuming substances such as acetol in the distillate were carried out in the same ways as described in the previous papers. (R. Nodzu, *loc. cit.*)

(4) During the course of evaporation, some iodine-consuming substance which has no reducing power for Fehling solution, was distilled. This distillate presents an interesting subject for research.

On further meticulous fractional crystallization of these precipitates from hot water, the followings were isolated: From I, diacetyl-bis-semicarbazone (m.p. 279–280°) and methylglyoxal-bis-semicarbazone (m.p. 262–264°); from II and III, mainly acetol semicarbazone (m.p. 197–198°), and pyruvic acid semicarbazone (m.p. 212–213°) and diacetyl-mono-semicarbazone (m.p. 227–228°) in a small quantity; from IV, lactic aldehyde semicarbazone (m.p. 246–247°) and acetol semicarbazone. Besides these semicarbazones, hydrazodicarbonamide (m.p. 257-258°) was isolated from II, III, and IV. These semicarbazones were all identified by the mixed melting point determinations. Another similar experiment at *p*H 6.2–6.6 was made with similar results, as will be seen in Table 1 in which the former results are also cited.

Table 1.

No.	Glucose g.	K-phosphate mixture 40%		Distillate c.c.	Iodine consuming substance as acetol g.	Semicarbazones g.				
		*p*H.	c.c.			m.p. 278°	m.p. 261°	m.p. 245°	m.p. 211°	m.p. 197°
1	200	5.2–5.6	1000	9000	4.92	0.1	0.05	0.06	0.02	5.51
2	200	6.2–6.6	1000	9000	5.18	0.08	0.06	0.08	0.01	4.40

Acetol and lactic aldehyde. Acetol (b.p. 53–54°/78mm.; semicarbazone m.p. 198–199°) was synthesized from monobromoacetone following A. Levene and A. Walti.[5] Lactic aldehyde (m.p. 105–107°; semicarbazone m.p. 245–247°, Found N. 32.24 Calc. for $C_4H_9O_2N_3$: N. 32%; 2.4-dinitrophenylhydrazone m.p. 154–155°) was prepared by hydrolysis of monobromacetal, following R. Dwarzak and W. Prodinger.[6] On treating with semicarbazide, the acetol gave only its semicarbazone and nothing of lactic aldehyde, and the lactic aldehyde also its semicarbazone only.

Thus it was confirmed that the acetol and the lactic aldehyde were free each from the other. The distillation of these substances with the phosphate solution and the analysis of distillates were carried out in the same ways as described in the case of glucose. The results of experiments are summerized in Tables 2 and 3.

Semicarbazones of methylglyoxal (m.p. 262–264°), lactic aldehyde (m.p. 246–247°) and acetol (m.p. 197–198°) in these tables, were respectively identified by the mixed melting point determination.

Table 2.

No.	Acetol g.	K-phosphate mixture 40%		Distillate c.c.	Iodine consuming substance as acetol g.	Semicarbazones g.		
		*p*H.	c.c.			m.p. 262°	m.p. 246°	m.p. 197°
1	1.0	5.2–5.6	100	1200	0.64	0.02	0.02	1.15
2	1.0	6.2–6.6	100	1200	0.68	0.03	0.02	1.25

(5) A. Levene and A. Walti, *Organic Syntheses*, Vol. **10** (1930), 1.
(6) R. Dwarzak and W. Prodinger, *Monatsh*, **48** (1927), 252; **50** (1928), 459.

Table 3.

No.	Lactic aldehyde g.	K-phosphate mixture 40%		Distillate c.c.	Iodine consuming substance as acetol g.	Semicarbazones g.		
		*p*H.	c.c.			m.p. 262°	m.p. 246°	m.p. 197°
1	0.5	5.2–5.6	100	1500	0.43	Trace	0.1	0.35
2	0.5	5.2–5.6	100	1500	0.43	Trace	0.08	0.32
3	0.5	6.2–6.6	100	1500	0.4	Trace	0.1	0.4

In conclusion the writer wishes to express his sincere thanks to Prof. Dr. R. Nodzu for his valuable suggestions throughout this work.

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The Influence of Temperature on the Formation of Platinum-carbonyl Sol.

By Isamu SANO.

(Received February 10, 1940.)

On passing carbon monoxide through a dilute aqueous solution of chloroplatinic acid at ordinary temperature, a colloidal solution of red colour is obtained in a short time, the general description of the formation and behaviour of the sol being given in the foregoing paper.[1] From various facts[1], [2] such as the oxidizing as well as decomposing action of air, oxygen and aqueous solution of bromine or hydrogen peroxide, the sol of red colour and the sol of black colour obtainable by dialyzing the red one or by letting it stand in the air, might be assumed to be composed of colloidal platinum-carbonyl and colloidal platinum respectively. The present paper deals with the influence of temperature together with concentration of the solution of chloroplatinic acid on the formation of the sol.

Experimental. Carbon monoxide was prepared by heating the mixture of formic acid and concentrated sulphuric acid and washed by bubbling it through alkaline hydroxide solutions. The aqueous solutions of

(1) I. Sano, this Bulletin, **9** (1934), 320.
(2) I. Sano, this Bulletin, **13** (1938), 118.

chloroplatinic acid were made by dissolving the acid ($H_2PtCl_6 \cdot 6H_2O$) from Takeda in ordinary distilled water. The reaction vessel used was cleaned, prior to use, with chromic acid mixture and, if necessary, with aqua regia and steamed with water vapour.

A 50 c.c. of the chloroplatinic acid solution of a definite concentration was taken in each run of the experiments. The gas was, by way of a pre-heating device constructed of glass-tube, introduced into it at the desired temperatures and at a rate of 3 litres per hour constant throughout the runs of experiment, from a capillary glass-tube having a diameter short of 1 mm.

Results and its discussion. The colour of the chloroplatinic acid solution turns, with the formation of colloidal solution, from pale yellow into red, brown as well as black according to the temperature and the concentration of the solution. The transitional change in colour of the solution was observed with the naked eye under day-light with simultaneous recording of time during the passage of carbon monoxide through the solution. Some of the results obtained are given in the following tables (Table 1 to Table 6 inclusive), where c stands for the concentration of the starting aqueous solution of the acid ($H_2PtCl_6 \cdot 6H_2O$) in per cent, θ the temperature of preparation in °C., t the time elapsed from the commencement in minutes and h the hue of the solution observed at time t.

As can be seen from the tables, the chloroplatinic acid solutions assume, through the stages as under stated, a variety of colours according to the temperature of reaction as well as the concentration of solution in consequence of the passage of carbon monoxide. The transitional change in colour of the solution in any run may be summarily outlined as follows: In the incipient stage, the solution will faintly assume a shade of a black tint in a short course of time from the start—this tendency will be perceived appreciably in concentrated solutions and promptly at high temperatures and may be supposed to be due to the transient formation of a lower salt like platinous chloride[1], [3] soluble in hydrochloric acid.[4] It will yield platinum carbonyl chloride in combination with carbon monoxide only to be so unstable in aqueous solution that it readily decomposes into platinum, carbon dioxide and hydrochloric acid—to be immediately followed by the colouration bearing brown as the predominant colour; this period being over, the solution will be of a tone of colour ranging from red to brown, and in the ultimate stage, will take, in accordance with the conditions concerned, a deep colour between purplish red and dark brown if observed in transmitted light, though tinged more or less deeply with black in reflected one. The colloidal solutions prepared from the acid solutions having larger concentrations such as 0.08 as well as 0.1% will be black in appearance and unstable, irrespective of the temperature of preparation, and settle in some measure presently after its formation. It was observed throughout the present experiment that

(3) F. C. Phillips, *Am. Chem. J.*, **16** (1894), 255.

(4) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 16, 251.

Table 1.

c: 0.02 θ: 20

t	h
0	pale yellow
16	faintly tinged with dark
20	faintly tinged with darkish red
23	light red with a mere dash of purple
30	red with a dash of purple
40	,,
60	,,

Table 2.

c: 0.02 θ: 50

t	h
0	pale yellow
9	faintly tinged with dark
11	light brown
17	brown with a dash of red
30	red having a tinge of brown
40	coloured more deeply
50	darkish red faintly tinged with brown
60	,,

Table 3.

c: 0.02 θ: 80

t	h
0	pale yellow
7	faintly tinged with dark
8	faintly tinged with darkish yellow slightly inclining to brown
10	light brown
25	tinged more deeply with dark
40	dark brown
60	,,

Table 4.

c: 0.08 θ: 20

t	h
0	light yellow
13	faintly tinged with dark
14	light yellow having a tinge of darkish red
16	brownish yellow with a mere dash of red
18	brown inclining to red
20	red with a tinge of brown
22	red with a dash of purple
60	,,

Table 5.

c: 0.08 θ: 50

t	h
0	light yellow
8	faintly tinged with dark
12	dark yellow
17	coloured more deeply
20	dark yellow with a dash of brown
40	dark brown slightly inclining to yellow
50	dark brown
60	,,

Table 6.

c: 0.1 θ: 20

t	h
0	light yellow
11	faintly tinged with dark
14	light brown slightly inclining to yellow
18	brown
19	brownish red faintly tinged with purple
21	red with a dash of purple
28	darkish red
40	darkish red with a tinge of brown
60	,,

the more dilute the starting acid solutions, the more stable were the sols obtained.

A summary of the hues, h, of colloidal solutions obtainable under sets of conditions concerning the concentration, c, of the chloroplatinic acid solution and the temperature, θ, at which the passage of carbon monoxide was performed is given in Table 7. The relations among them are plotted on a graph with the values of the temperature, θ, in °C. as ordinates and of the concentration, c, in % as abscissæ in Fig. 1.

Table 7.

c: 0.01

θ	h
5	red with a dash of purple
20	,,
35	,,
50	brownish red with a mere dash of purple
55	red slightly tinged with brown
60	brown with a tinge of red
65	brown
80	dark brown

c: 0.02

θ	h
5	red with a dash of purple
20	,,
35	,,
50	darkish red faintly tinged with brown
55	darkish red with a tinge of brown
60	brown
65	dark brown
80	,,

c: 0.05

θ	h
5	red with a dash of purple
20	,,
35	,,
50	brown with a tinge of red
55	brown
60	dark brown
65	,,

c: 0.08

θ	h
20	red with a dash of purple
25	brownish red faintly tinged with purple
35	brown slightly inclining to red
40	brown
50	dark brown

c: 0.1

θ	h
5	red with a dash of purple
15	,,
20	darkish red with a tinge of brown
30	brown with a mere dash of red
35	brown
45	,,
50	dark brown

It is no wonder that the boundaries between the domains of hue should be somewhat wanting in clearness, the lines of demarcation, a, b and c, though drawn well-definedly in the figure, only indicating the approximate positions of them. It can be seen from the figure that a colloidal solution assuming red with a dash of purple will be produced at ordinary

temperatures from the chloroplatinic acid solution of lower concentration; the domain of its formation is reduced with the increasing concentration of the starting solution and extinguished at a limiting concentration,

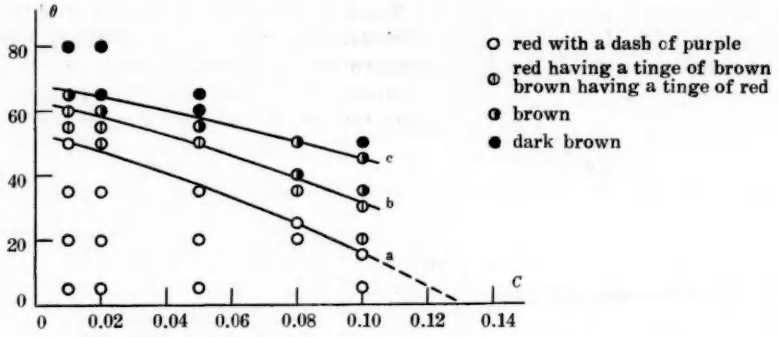

Fig. 1.

$c = 0.13$, as shown by the extension of the line a, and it points to the supposition, therefore, that there should be never produced stable sols of red inclining to purple beyond the limiting concentration at any temperature. F. C. Phillips[3] observed that aqueous solutions of platinum chloride were slightly tinged with black by the action of carbon monoxide, cold or at 100°C., to be subsequently followed by slow deposition of metallic platinum.

With the intention of acquiring further informations on the colouration effects above mentioned, the extinction coefficients of the sols were measured after they were left at room temperature out of contact with the air for the space of 2 hours from the close of preparation downward. The measurements were made with the Nutting's spectrophotometer at ordinary temperature, in that the extinction coefficient, ε, could be estimated with the aid of the formula

$$\varepsilon = -2 \log (\cos \alpha)/c \cdot d,$$

where α denotes the angle of extinction for any visible ray to be determined through observation with the spectrophotometer, c the concentration and d the thickness of layer of the solution. The results obtained are diagrammatically depicted in Fig. 2, 3, 4, 5 and 6 in terms of the relationship between the extinction coefficient multiplied by the concentration, εc, per unit thickness in cm. of the sols concerned and the wavelength of the rays referred, λ, in mμ in company with the temperatures of preparation of the sols, θ, in °C. εc was taken in place of c on account of certain difficulties attending on the determination of concentration of the sols owing to their variability in the air. This will suffice to give informations on the extinction effects of the sols obtainable from the acid solution of one and the same concentration.

The dotted line in Fig. 6 represents the relation between εc and λ for a 0.1% solution of chloroplatinic acid; as compared with this, it is obvious for the colloidal solution to display a larger extinction effect.

The sols will turn black in due time, as already descibed,[1] by leaving it intact in the air owing to the disappearance of carbon monoxide or carbonyl group from colloidal particle due to volatilization towards as well as oxidation by the air. It might be considered for the extinction coefficient of the sol to exhibit a definite increase in magnitude as a consequence of the change in colour, this being manifestly indicated through the results given as the thick lines, full for the red sol as well as broken for the black one in Fig. 3.

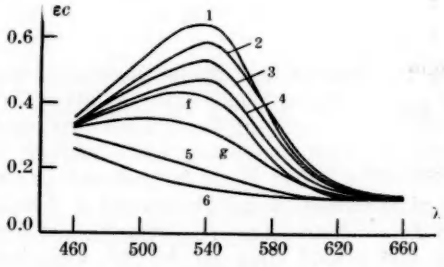

Fig. 2.

Curve	θ
1	5
a	15
2	20
b	25
c	30
3	35
d	40
e	45
4	50
f	55
g	60
5	65
6	80

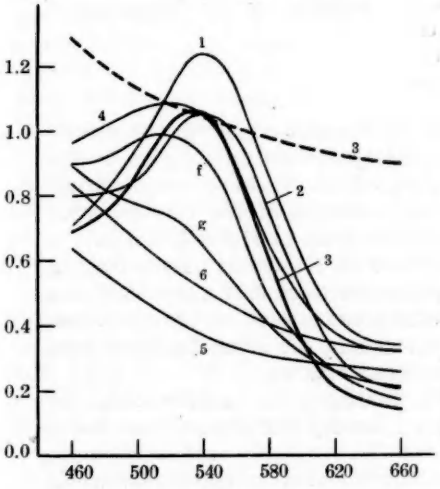

Fig. 3.

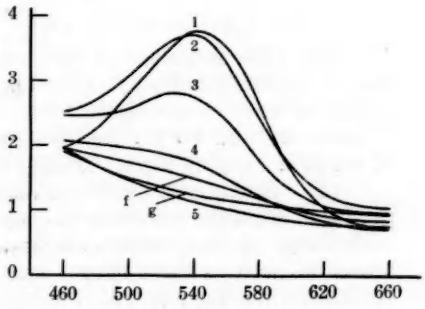

Fig. 4.

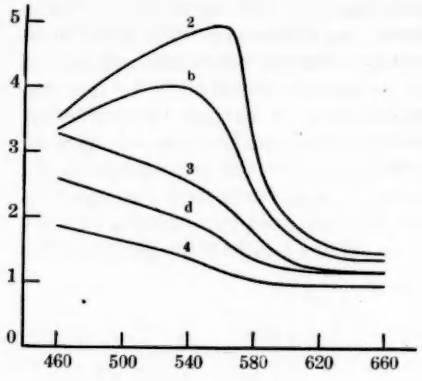

Fig. 5.

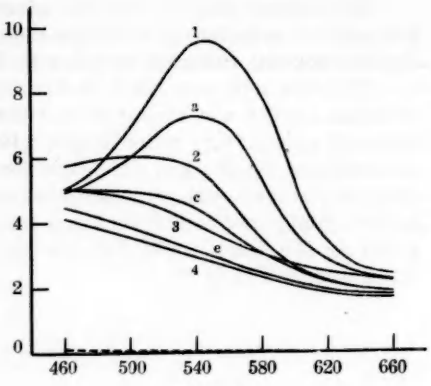

Fig. 6.

It can be distinctly seen from the figures that the extinction curves for the sols having a tinge of red reach a definite maximum at about 540 mμ; while the curves for those with a tinge ranging from brown to black show monotonously decreasing gradient with increasing wave-length. It would seem, therefore, that the extinction effect could be reduced as the temperature of formation of the sol is raised, although beyond a certain limiting temperature depending on the concentration of solution this should attain a noticeable magnitude for the second time as the chloroplatinic acid solution passes immediately into a sol tinged with black by the action of carbon monoxide at higher temperatures as indicated in Fig. 1.

It must be added that the run of the extinction curves was taken into consideration in discriminating the shade and tone of a colour of the sol produced and establishing the influence of the temperature of preparation and the concentration of chloroplatinic acid solution on the formation of it as represented in Fig. 1.

Summary.

(1) The influence of the temperature of preparation on the formation of platinum-carbonyl sol from the chloroplatinic acid solution by the action of carbon monoxide were investigated at various temperatures between 5° and 80°C., together with the influence of the concentration of solution ranging from 0.01 to 0.1% with respect to $H_2PtCl_6 \cdot 6H_2O$.

(2) Stable sols having a tinge of red with a dash of purple may be produced from the solutions of concentrations between 0.01 and 0.08% in a wide range of temperature; sols of various colours such as brownish red, brown as well as dark brown may be formed in the same limits of concentration as the above at the elevated temperatures.

(3) Sols tinged with red slightly inclining to purple may be obtained, though unstable, from the 0.1% acid solutions only at lower temperatures.

(4) The colouration effects above-mentioned were spectroscopically analyzed with the Nutting's spectrophotometer, and it was found that

the extinction curves for the sols tinged with red reach a maximum at about 540 mμ, while those for the sols with a tinge varying from brown to black decrease monotonously with the increasing wave-length.

The author wishes to express his hearty thanks to Prof. J. Sameshima for his kind guidance in the present experiment. It is also his pleasant duty to acknowledge the valuable advice offered by Dr. K. Yamasaki.

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The Effect of Reduced Nickel on the Addition of Hydrogen Bromide to Undecenoic Acid in Various Solvents.

By Matsuji TAKEBAYASHI.

(Received February 24, 1940).

In the previous work with Y. Urushibara[1] it was established that, while hydrogen bromide adds to pure undecenoic acid in toluene solution in the absence of oxygen to yield nearly pure 10-bromoundecanoic acid, the presence of reduced nickel reverses the direction of addition to some extent and, for instance, about one-third of the product formed in moderately dilute toluene solution is 11-bromoundecanoic acid (oxygen is far more potent in producing the same effect). In the previous experiments toluene was used exclusively as the solvent. The present paper records the results of the additions in the presence of reduced nickel in various solvents, which are summarized in the accompanying table.

Hydrogen bromide was passed into a solution of 1.0 g. undecenoic acid in 15 c.c. of the solvent in the presence of 2.3 g. of reduced nickel at 0°C. in the dark for one hour. The mixture was left to stand overnight and the product was examined. The reaction was always complete. The proportion of 10- and 11-bromoundecanoic acids in the reaction product was determined by observing the melting (clearing) point.

In benzene, toluene, ligroin, and carbon tetrachloride, reduced nickel suffered no change during the reaction, and the effect was as marked as previously observed in toluene (somewhat smaller in ligroin) (Exp. 1, 2, 3 and 7). On the other hand, in acetic acid and ether reduced nickel was attacked seriously by hydrogen bromide, the solution being coloured greenish, and the effect of the metal was found very weak (Exp. 4 and 5). In chloroform, the metal was attacked slightly but the solution was not

(1) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 331, 404, 574.

Exp. No.	Solvent	Product	
		Melting point (°C.)	11-Bromo-acid (%)
1	Benzene	26.0	33
2	Toluene	25.8	33
3	Ligroin	27.3	28
4	Acetic acid	32.0	12
5	Ether	(liquid)	
6	Chloroform	29.8	20
7	Carbon tetrachloride	26.0	33

coloured, and the proportion of 11-bromo-acid in the product was intermediate (Exp. 6). These results appear to be in harmony with the previous experiences in the addition of hydrogen bromide to allyl bromide that the abnormal (reversely directed) addition was caused only by the metallic surface of the ferromagnetic metals, viz., nickel and iron, whereas their salts, viz., ferric chloride added,[2] nickel bromide formed in case of the contamination of the metal by its oxide,[3] and cobalt bromide produced owing to the little resistance of metallic cobalt to the attack by hydrogen bromide,[3] promoted the normal addition. However, in view of the fact that the action of oxygen on the addition of hydrogen bromide to undecenoic acid was impeded in acetic acid and ether,[4] the effect of reduced nickel might not be allowed to appear even if the metal were not attacked by hydrogen bromide in these solvents.

Experimental.

Materials. Undecenoic acid used was a commercial product (Kahlbaum, "extra pure") melting at 23.8° (corr.) and can be regarded fairly pure. It gave no colouration with ammonium thiocyanate and ferrous ammonium sulphate, being free from peroxide. Hydrogen bromide was generated by the action of bromine on hot tetralin, passed through cooled tetralin, over anhydrous calcium bromide and anthracene, and through a tube cooled with ice and salt, condensed in a vessel cooled with solid carbon dioxide and ether, and vaporized, the middle fraction only being used. Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at 350–400°C. and reduced again in the atmosphere of hydrogen at 350°C. in the reaction tube.

Benzene and toluene, free from thiophene, were redistilled over metallic sodium. Ligroin was washed with sulphuric acid, aqueous sodium carbonate, and water, dried over calcium chloride, and distilled over sodium (boiling point 80–95°C.). Acetic acid was refluxed with 2% of its weight of potassium permanganate, distilled, dried over phosphorus pentoxide, and purified by fractional distillation. Ether was washed repeatedly with concentrated sulphuric acid until the latter remained colourless, shaken with an alkaline aqueous solution of potassium permanganate, washed with water, dried over calcium chloride, and distilled. The ether purified in this way was free from peroxide. Chloroform was shaken several times with about half its volume of water and then dried over calcium chloride, and distilled over phosphorus pentoxide. Carbon tetrachloride was refluxed with an alkaline solution of potassium permanganate, washed with water, dried over calcium chloride, distilled, and redistilled with the addition of phosphorus pentoxide.

(2) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.
(3) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 755; **12** (1937), 51.
(4) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.

Apparatus and Experimental Procedures. The main part of the apparatus consists of a reaction tube (R) of 22 mm. diameter and 100 c.c. capacity, a side tube (S) of 22 mm. diameter and 90 c.c. capacity an inlet tube (I) for hydrogen bromide and hydrogen, and an outlet (O) for excessive hydrogen bromide and for evacuation. The whole is made of Pyrex glass.

Undecenoic acid (1.0 g.) was dissolved in a required amount (15 c.c.) of the solvent in S, the volume of the solution was marked on S, and further 5 c.c. of the solvent was added. Reduced nickel was placed in R. The whole system was evacuated at room temperature. Thus the excess of the solvent was distilled off through O. In this way air was driven out. When the volume of the solution reached the mark, the solution was frozen by cooling in liquid air while the nickel in R was heated to 350°C., evacuation being continued. The stopcock of O was closed, hydrogen introduced from I, and after a while the vessel evacuated again. This process was repeated several times, cooling of S and heating of R being continued. Then R was cooled to room temperature under evacuation. O was closed, and S taken out of liquid air. Then the solution in S was decanted on reduced nickel in R, and hydrogen bromide introduced.

Hydrogen bromide was passed at 0°C. in the dark for one hour. The mixture was left to stand at room temperature in the dark overnight. The solvent and the excess of hydrogen bromide were removed in vacuum at 50°C., and the remaining substance was collected with the solvent. The nickel was filtered off and washed with the solvent. The solution was again evaporated in vacuum at 60°C. The product was always obtained in quantitative yield, and did not decolourize bromine. The product was cooled to crystallization and pressed on cooled porous plates.

The proportion of 10- and 11-bromoundecanoic acids in the reaction product was determined by observing the melting (clearing) point. For this purpose the data of Ashton and Smith[4] for the binary mixtures of the two bromo-acids were employed.

The author expresses his hearty thanks to Prof. Y. Urushibara of the Imperial University of Tokyo for his kind guidance and to Prof. K. Ishikura, the director of the Osaka Higher School, for his encouragement. Thanks are also due to the Imperial Academy of Japan and to Hattori Hoko Kwai for grants.

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The Influences of Aldehydes and Hydroxyaldehydes on the Addition of Hydrogen Bromide to Undecenoic Acid in Presence and in Absence of Oxygen or Reduced Nickel.

By Matsuji TAKEBAYASHI.

(Received February 24, 1940).

While hydrogen bromide adds to undecenoic acid in benzene or toluene solution under the normal conditions to yield nearly pure 10-bromoundecanoic acid, oxygen[1] and reduced nickel[2][3][4] reverse the direction of addition to give rise to the formation of more or less 11-bromoundecanoic acid. Impurities in the undecenoic acid originating in the preparation of the acid from ricinus oil increase the sensitiveness of the acid to oxygen,[1][5] while the effect of reduced nickel appears not to be influenced by the impurities.[5] On the other hand, antioxidants such as catechol and hydroquinone inhibit the actions of both oxygen and reduced nickel.[3] Ashton and Smith[1] showed that *a*-heptenylheptaldehyde formed by the action of alcoholic potash on heptaldehyde was a powerful agent to make undecenoic acid sensitive to oxygen and suggested that the heptaldehyde formed during the distillation of ricinus oil must be the origin of the powerful agent in the impure undecenoic acid.

The author has examined the influences of some aldehydes and hydroxyaldehydes, with a view to seeing if there could be a substance capable of exhibiting opposite influences on the effects of oxygen and of reduced nickel, but without finding any. Benzene instead of toluene was used as the solvent throughout the experiments described below, because it has been shown that they give similar results.[1][4]

The effects of some aldehydes alone on the addition were first examined. Hydrogen bromide was passed into a solution of pure undecenoic acid (1.0 g.) in benzene (15 c.c.) with the addition of the aldehyde (25 mols % to the acid) at 0°C. in the dark for one hour. The mixture was allowed to stand at room temperature in the dark overnight. The reaction was always complete. The composition of 10- and 11-bromoundecanoic acids in the product was determined from the melting (clearing) point as previously. The results are given in Table 1. Compare them with the data quoted in Table 2 from the previous work.

Propylaldehyde, benzaldehyde and salicylaldehyde, which were practically free from peroxides, exhibited but a small influence, if any, on the addition of hydrogen bromide to undecenoic acid (Exp. 1, 3, and 4). On the other hand, the crotonaldehyde used contained peroxide, and accordingly the direction of addition was reversed to some extent (Exp. 2).

1) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.
2) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 331.
3) *Idem, ibid.*, **13** (1938), 404.
4) M. Takebayashi, *ibid.*, **15** (1940), 113.
5) Y. Urushibara and M. Takebayashi, *ibid.*, **13** (1938), 574.

Table 1.

Exp. No.	Aldehyde	Product	
		Melting point (°C.)	11-Bromo-acid (%)
1	Propylaldehyde, 0.1 g.	33.0	8
2	Crotonaldehyde containing peroxide, 0.1 g.	29.0	23
3	Benzaldehyde, 0.15 g.	33.2	8
4	Salicylaldehyde, 0.2 g.	33.3	7

Table 2. Undecenoic acid 3.68 g. in the first two exp., 2.5 g. in others. Toluene, 20 c.c.

In presence of	Product	
	Melting point (C.)	11-Bromo-acid (%)
None (vacuum)	34.7	1
Air	48.7	97
Reduced nickel, 3.0 g.	25.5	34
Air+Catechol, 0.3 g. (22 mols %)	33.5	6
Reduced nickel, 3.0 g.+Catechol, 0.3 g.	33.0	8
Air+Hydroquinone, 0.3 g. (22 mols %)	34.2	3
Reduced nickel, 3.0 g.+Hydroquinone, 0.3 g.	32.6	10

The influences of aldehydes and hydroxyaldehydes on the effects of oxygen and reduced nickel were then examined. The results are summarized in Table 3. Hydrogen bromide was passed into a solution of

Table 3.

Exp. No.	In presence of	Product	
		Melting point (°C.)	11-Bromo-acid (%)
5	Air+Benzaldehyde, 0.15 g.	47.4	92
6	Reduced nickel, 2.3 g.+ Benzaldehyde, 0.15 g.	26.3	32
7	Air+Salicylaldehyde, 0.2 g.	47.2	91
8	Reduced nickel, 2.3 g.+ Salicylaldehyde, 0.2 g.	26.2	32
9	Air+Protocatechualdehyde, 0.2 g.	35.5	52
10	Reduced nickel, 2.3 g.+ Protocatechualdehyde, 0.2 g.	29.2	22
11	Air+Vanillin, 0.2 g.	42.2	72
12	Reduced nickel, 2.3 g.+ Vanillin, 0.2 g.	29.0	23

pure undecenoic acid (1.0 g.) in benzene (15 c.c.) at 0°C. in the dark in the presence of the aldehyde (25 mols % to the acid) and either air (Exp. 5, 7, 9, and 11) or reduced nickel (2.3 g.) (Exp. 6, 8, 10, and 12). Compare the results with Table 2.

Benzaldehyde and salicylaldehyde exhibited negligibly small influences on the actions of oxygen and of reduced nickel (Exp. 5, 6, 7, and 8). Protocatechualdehyde and vanillin exerted weak but noticeable inhibiting influences on the actions of both oxygen and reduced nickel (Exp. 9, 10, 11, and 12). Their inhibiting actions, however, were found far smaller than those of catechol and hydroquinone (compare Table 2).

Experimental.

Materials. Undecenoic acid, reduced nickel, hydrogen bromide, and benzene were the same as described in the previous paper.(1) Propylaldehyde (Kahlbaum, "extra pure") was distilled carefully on the day of use. It gave a very faint colouration with ammonium thiocyanate and ferrous ammonium sulphate, being almost free from peroxide. Crotonaldehyde used was a commercial product containing peroxide in a quantity. Benzaldehyde, a pure product, was distilled in vacuum and used immediately. Salicylaldehyde, a commercial pure material, was distilled in vacuum. It was free from peroxide. Protocatechualdehyde and vanillin were commercial specimens (Kahlbaum, "extra pure") melting at 152° and 80.5°, respectively.

Apparatus and Experimental Procedures. The apparatus was the same that was used in the previous work.(1) In experiments in the presence of aldehydes, undecenoic acid (1.0 g.) and the aldehyde (25 mols % to the acid) were dissolved in a required amount (15 c.c.) of benzene and further 5–6 c.c. of benzene was added. The excess of benzene was distilled off in vacuum at room temperature. In this way air was driven out. Hydrogen bromide was passed into the solution at 0°C. in the dark for an hour. The mixture was left to stand overnight at room temperature in the dark. The reaction mixtures were coloured. The solvent, the aldehyde, and the excess of hydrogen bromide, were removed in vacuum at 60°, and the remaining substance was collected with benzene. The solution was washed with water, dried over calcium bromide, decolourized with animal charcoal, and evaporated in vacuum at 60°.

In the additions in the presence of air and aldehydes, undecenoic acid and the aldehyde were dissolved in benzene. Protocatechualdehyde and vanillin were sparingly soluble in benzene and mostly remained undissolved. Hydrogen bromide was passed into the solution with cooling in ice water for one hour. The reaction mixture was treated as mentioned above. Salicyladehyde was driven out by evacuation. Protocatechualdehyde and vanillin remaining as coloured solids in the solutions were filtered off at 0°C. after hydrogen bromide had been removed in vacuum.

In experiments with reduced nickel and aldehydes, undecenoic acid and the aldehyde were dissolved in benzene beforehand, and the experiments were carried out in the same way as described in the previous paper.(1) The reaction mixture was treated as mentioned above.

The reaction was always complete and the product did not decolourize bromine. The composition of the product was determined from the melting point as previously.

The author expresses his hearty thanks to Prof. Y. Urushibara of the Imperial University of Tokyo for his kind guidance and to Prof. K. Ishikura, the director of the Osaka Higher School, for his encouragement. Thanks are also due to the Imperial Academy of Japan and to Hattori Hoko Kwai for grants.

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